A HEYWOOD PUBLICATION

British Chemical Engineering

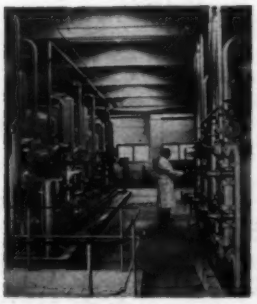
THE JOURNAL DEVOTED TO THE TECHNIQUES OF CHEMICAL ENGINEERING APPLIED TO INDUSTRY

OCTOBER 1959
Vol. 4 No. 10

Editor:
J. O. S. MACDONALD, B.Sc., A.R.I.C., A.M.I.Chem.E.

Associate Editor:
I. BERKOVITCH, Ph.D., F.R.I.C., A.M.I.Chem.E.

Assistant Editor:
WILLIAM D. CLIFFORD



A Boby three-stage demineralisation plant, capacity 24,200 gph, installed in a large pulp mill in Finland to treat feed water for high-pressure boilers.

Classified Advertisements — pp. 126-127

BRITISH CHEMICAL ENGINEERING is published monthly by HEYWOOD & CO. LTD., Drury House, Russell Street, Drury Lane, London, W.C.2 (Tel.: TEMple 3422), on the 20th of the preceding month. Annual subscription £2 U.K., £2 10s. 0d. sterling overseas for 12 issues post free ($7.50 U.S.A. and Canada) or by standing order through newsagents at 2s. 6d. a copy net. BRANCH OFFICE: Royal Buildings, 2 Mosley Street, Manchester, 2. Tel.: Central 9935 © Heywood & Co Ltd., 1959. Must not be reproduced without written permission.

MAIN ARTICLES

Principles and Practice of Ion Exchange *by T. R. E. Kressman, Ph.D., D.I.C., F.R.I.C.* 510

Les principes et la pratique d'échange des ions

Grundsätze und Anwendung von Ionenaustausch

Принципы и практика ионного обмена

Large-Scale Demineralisation of Sea and Brackish Water—Part 2 *by A. M. Eshaya, D.Eng., and B. F. Dodge, B.Sc.* 516

La déminéralisation sur grande échelle de l'eau de mer et de l'eau saumâtre — Partie 2

Grossangelegte Entmineralisierung von See- und Brackwasser

Крупномасштабная деминерализация морских и солоноватых вод—Часть 2

High Pressure Chemistry—Part 2 *by W. Strauss, M.E., M.Sc.* 521

Le traitement chimique à haute pression — Partie 2

Die chemische Bearbeitung unter Hochdruck — 2 Teil

Химическая обработка под высоким давлением — Часть 2.

Porosity Determination of Fluidised Beds *by Dr. Ir. P. J. Bakker and Prof. Dr. Ir. P. M. Heertjes* 524

La determination de la porosité d'un lit fluidisé

Die Bestimmung der Porosität eines Wirbelbetts

Определение пористости разжиженных слоев

Speculative Pilot Design and Scale-up—Part 1 *by Dr. Donald Q. Kern* 530

Extrapolation des installations chimiques

Fragen der Grössenextrapolation bei chemischen Anlagen

Проблемы химических установок при переходе от одного агрегата к другому большего размера.

Fission Product Waste from Reactors—Processing of Highly Active Solutions *by T. V. Healy, M.Sc., A.R.I.C.* 538

Les déchets de fission dans les reacteurs: traitement des solutions hautement radioactives

Abfallprodukte der Spaltung in Reaktoren: Behandlung von Hochreaktiven Lösungen

Отбросы расщепления: обработка высокоактивных растворов

OTHER FEATURES

Leader: Petroleum Chemicals Thriving 509

Rolling Extruder for Pretreatment of Pastes Prior to Drying 515

A Film of Catalytic Reforming 529

Electronic Computer in Commerce 534

An International Conference on Chemical Engineering 535

Radiation Sources for Chemical Processes 542

Mass Transfer on Bubble-Cap and Sieve Plates 544

Nomogram: Heat-Transfer Coefficients for Steam Condensing on Vertical Tubes by D. S. Davis 546

American Letter: The Cost of Progress 550

REGULAR FEATURES

Digest 503
Process Engineer's Notebook 548
World of Chemicals 552
Book Reviews 554
Plant Equipment News 558
Month's News in Brief ... 568

Résumés

B.C.E., 4, 10, 510. U.D.C. No. 66.094.94.

LES PRINCIPES ET LA PRATIQUE D'ÉCHANGE DES IONS

par T. R. E. Kressman

On résume les techniques d'échange des ions et leurs applications. Leur importance dans la récupération de materiaux de haut prix telles que le uranium et des méthodes d'opération : colonne à chargement périodique, colonne à lits mixtes, appareils à operation continu et l'électrodialyse, sont indiqués.

B.C.E., 4, 10, 516. U.D.C. No. 66.064 : 551. 464 : 551.481.

LA DÉMINÉRALISATION SUR GRANDE ECHELLE DE L'EAU DE MER ET DE L'EAU SAUMÂTRE — PARTIE 2

par A. M. Eshaya et B. F. Dodge

On résume les principes de la déminéralisation de l'eau de mer et de l'eau saumâtre par moyen de membranes ; la rentabilité, les problèmes d'exploitation et les potentialités sont indiqués.

B.C.E., 4, 10, 521. U.D.C. No. 66.987.

LE TRAITEMENT CHIMIQUE À HAUTE PRESSION — PARTIE 2

par W. Strauss

Cet article résume quelques effects des pressions extrêmement élevées sur les réactions chimiques et physiques. On traite de la vélocité de quelques réactions ioniques à phase-liquide ainsi que les réactions dans lesquelles la vélocité est déterminée par la formation d'un radical libre.

B.C.E., 4, 10, 524. U.D.C. No. 66.096.5 : 537.226 : 539.217.1.

LA DETERMINATION DE LA POROSITÉ D'UN LIT FLUIDISÉ

par P. J. Bakker et P. M. Heertjes

Pour déterminer la porosité d'un lit fluidisé il faut établir une relation entre la constante diélectrique mesurée et la porosité. Les auteurs développent une telle relation qui obéit à la loi de Wiener. On démontre que cette loi est valable pour des mélanges de billes de verre et d'air. La méthode possède un interêt en rapport avec d'autres expériences dans lesquelles il faut mesurer les constantes diélectriques d'un mélange.

B.C.E., 4, 10, 530. U.D.C. No. 66.013.5.

EXTRAPOLATION DES INSTALLATIONS CHIMIQUES

par D. Q. Kern

Cet article donne une analyse mathématique qui employée en combinaison avec des expériences pratiques, peut servir à l'étude de l'extrapolation. On donné aussi une critique de la théorie des modèles.

B.C.E., 4, 10, 538. U.D.C. No. 621.039.431:662.73

LES DÉCHETS DE FISSION DANS LES REACTEURS : TRAITEMENT DES SOLUTIONS HAUTEMENT RADIOACTIVES

par T. V. Healy

Ce sommaire des méthodes existantes d'évacuation des déchets radioactifs met en relief le problème des isotopes à longue vie Cs^{137} et Sr^{90}. La récuperation des métaux rares tels que Ru et Tc contenus dans des solutions à longue vie est également discutée. Enfin, l'auteur se penche sur les caractères d'un procédé integral pour le traitement des déchets.

Kurzreferate

B.C.E., 4, 10, 510. U.D.C. No. 66.094.94.

GRUNDSÄTZE UND ANWENDUNG VON IONENAUSTAUSCH

von T. R. E. Kressman

Eine Übersicht der Ionenaustauschverfahren und ihrer Anwendungen. Auf ihre Benutzung für die Rückgewinnung von wertvollen Materialen wie Uran und auf Arbeitsprozesse der folgenden Typen : diskontinuierliche Kolonnen, Mischbettkolonnen, kontinuierliche Methoden und Elektrodialyse, wird hingewiesen.

B.C.E., 4, 10, 516. U.D.C. No. 66.064 : 551. 464 : 551.481.

GROSSANGELEGTE ENTMINERALISIERUNG VON SEE- UND BRACKWASSER

von A. M. Eshaya und B. F. Dodge

Eine Übersicht der Arbeitsweise von Membranprozessen für die Entmineralisierung von See- und Brackwasser. Wirtschaftlichkeit, Betriebsprobleme und Aussichten werden besprochen.

B.C.E., 4, 10, 521. U.D.C. No. 66.987.

DIE CHEMISCHE BEARBEITUNG UNTER HOCHDRUCK — 2. TEIL

von W. Strauss

Eine Übersicht einiger Einflüsse von Höchstdrücken auf chemische und physische Reaktionen. Die Geschwindigkeit von verschiedenen Flüssigkeitsphasereaktionen wird behandelt sowie Reaktionen wo die Geschwindigkeit von der Entstehung eines freien Radikals abhängig ist.

B.C.E., 4, 10, 524. U.D.C. No. 66.096.5 : 537.226 : 539.217.1.

DIE BESTIMMUNG DER POROSITÄT EINES WIRBELBETTS

von P. J. Bakker und P. M. Heertjes

Zur Bestimmung der Porosität eines Wirbelbetts muss man das Verhältnis zwischen der gemessenen Dielektrizitätskonstante und der Porosität kennen. Ein derartiges Verhältnis wird von den Verfassern vorgeschlagen ; sie wird dem Wiener'schen Gesetz untersetzt. Die Gültigkeit dieses Verhältnisses im Falle von einer Glaskugel-Luft-Mischung wird bewiesen. Die Methode kann auch für andere Versuche, die die Bemessung der Dielektrizitätskonstante einer Mischung benötigen, angewendet werden.

B.C.E., 4, 10, 530. U.D.C. No. 66.013.5.

FRAGEN DER GRÖSSENEXTRAPOLATION BEI CHEMISCHEN ANLAGEN

von D. Q. Kern

Verfasser beschreibt eine mathematische Behandlungsweise die, mit praktischen Versuchen kombiniert, bei der Grössenextrapolation verwendet werden kann. Der Aufsatz schliesst eine Kritik der Modelltheorie ein.

B.C.E., 4, 10, 538. U.D.C. No. 621.039.431:662.73

ABFALLPRODUKTE DER SPALTUNG IN REAKTOREN : BEHANDLUNG VON HOCHREAKTIVEN LÖSUNGEN

von T. V. Healy

In der vorliegenden Übersicht der verfügbaren Verfahren zur Abführung von radioaktiven Abfällen wird das Problem der langlebigen Isotopen Cs^{137} und Sr^{90} hervorgehoben. Die Rückgewinnung von seltenen Metallen wie z.B. Ru und Tc wird ebenfalls erläutert. Schliesslich bespricht der Autor die Merkmale eines Integralverfahrens zur Behandlung von Abfallprodukten.

Резюме

B.C.E., 4, 10, 510. U.D.C. No. 66.094.94.

ПРИНЦИПЫ И ПРАКТИКА ИОННОГО ОБМЕНА

Т. Р. Е. Кресман.

Краткий обзор техники ионного обмена и ее применения. В статье даются ссылки на ее значение для регенерирования таких ценных веществ, как уран, и разные методы ее использования, например : периодическая колонна, смешанослоевая колонна, непрерывная колонна и электродиализ.

B.C.E., 4, 10, 516. U.D.C. No. 66.064 : 551. 464 : 551.481

КРУПНОМАСШТАБНАЯ ДЕМИНЕРАЛИЗАЦИЯ МОРСКИХ И СОЛОНОВАТЫХ ВОД ЧАСТЬ 2

А. М. Ешая и Б. Ф. Додж.

Краткий обзор принципа действия мембранных процессов для деминерализации морской или солоноватой воды с последующей оценкой их экономики, эксплоатационных задач и возможностей

B.C.E., 4, 10, 521. U.D.C. No. 66.987.

ХИМИЧЕСКАЯ ОБРАБОТКА ПОД ВЫСОКИМ ДАВЛЕНИЕМ ЧАСТЬ 2

В. Страуе.

Краткий обзор некоторых влияний очень высоких давлений на химические и физические изменения. Рассматриваются скорости ионных жидкофазных реакций, а также реакции, в которых образование свободного радикала является фактором, определяющим скорость.

B.C.E., 4, 10, 524. U.D.C. No. 66.096.5 : 537.226 : 539.217.1.

ОПРЕДЕЛЕНИЯ ПОРИСТОСТИ РАЗЖИЖЕННЫХ СЛОЕВ

П. Ж. Баккэр и П. М. Хеертчес.

Для определения пористости разжиженного слоя необходимо знать зависимость измеряемой диэлектрической постоянной от пористости. Авторами разрабатывается такая зависимость и установлено, что она подчиняется закону Винера. Показано, что эта зависимость правильна для смесей стеклянных шаров и воздуха. Способ пригоден для других опытов, в которых необходимо измерение диэлектрических постоянных смеси.

B.C.E., 4, 10, 530. U.D.C. No. 66.013.5.

ПРОБЛЕМЫ ХИМИЧЕСКИХ УСТАНОВОК ПРИ ПЕРЕХОДЕ ОТ ОДНОГО АГРЕГАТА К ДРУГОМУ БОЛЬШЕГО РАЗМЕРА

Д. Кю. Керн.

В статье дается математический анализ, который совместно с опытами можно употреблять для задач, связанных с переходом от одного агрегата к другому большего размера. Дается также критика теории моделей.

B.C.E., 4, 10, 538. U.D.C. No. 621.039.431:662.73

ОТБРОСЫ РАСЩЕПЛЕНИЯ: ОБРАБОТКА ВЫСОКОАКТИВНЫХ РАСТВОРОВ

Т. В. Хили.

В настоящем обзоре имеющихся способов удаления радиоактивных отбросов подчеркивается проблема долгоживущих изотопов Cs^{137} и Sr^{90}. Также рассматривается извлечение редких металлов, так напр. Ru и Tc, из долгоживущих растворов. Наконец, автор обсуждает подробности интегрированного процесса обработки отбросов.

DIGEST OF INDUSTRIAL AND TECHNICAL DEVELOPMENTS

Semi-automatic Micro Reactor

FURTHER developments have been reported—resulting from a Mellon Institute Fellowship on petroleum—in microcatalytic-chromatographic technique for studying catalytic reactions. W. KEITH HALL, D. S. MACIVER and H. P. WEBER have now put these kinetic studies on a nearly automatic basis.

Earlier stages of this work have been described in a series of papers.* Gaseous or liquid hydrocarbon reactants were injected by hypodermic syringe into a carrying-gas stream passing over a catalyst in an 8 mm. O.D. reactor tube and then directly through a chromatographic column. This procedure was made more nearly quantitative in later work by the substitution of a dosing device consisting of a combination of stopcocks.

In general, the microcatalytic method has a number of advantages over more conventional procedures. The most important of its limitations is that when a small slug of the reacting mixture is carried through a bed of catalyst by a stream of inert gas, it is doubtful whether equilibrium or steady state assumptions can be made with respect to either the condition of the catalyst or the adsorption of the gases present. This may make it difficult, or perhaps impossible, to interpret results such as those for the pressure dependence of the reaction rate. Further, the data obtained are integral reaction rates, and the technique is not easily adaptable to the requirements for differential reaction kinetics. These factors have suggested that gas phase chromatography might be applied as an analytical tool in a more conventional manner, for example as a means of analysing the tail gas from a steady state, flow type reactor. In the earlier work, almost as much time was involved in measuring the chromatographic records obtained as in carrying out the actual experiments. Consequently, an automatic integrating device was developed. This allowed the areas of the various chromatographic peaks to "print out" in digital form. The latest report of this series issued by the Institute describes the "nearly automatic" version of the apparatus showing the utility of the resulting instrument, not only for the microcatalytic (slug) technique, but also for the more conventional use of GPC as noted above. The reactions studied were the polymerization of propylene and the cracking of 2,3-dimethylbutane over silica-alumina cracking catalysts.

J. Am. Chem. Soc. 1955, *Vol.* 77, *p.* 5860 *and* 1957, *Vol.* 79, *p.* 2091. *J. Phys. Chem. In the Press.* *Science*, 1957, *Vol.* 126, *p.* 821.

Using Large Radiation Sources for Industrial Chemical Processes

AN historic stage in development was represented by the decision of the International Atomic Energy Agency to call a conference on application of large radiation sources in industry. For this recent gathering in Warsaw was convened to discuss especially the application of such sources to industrial chemical processes. More than forty papers from eleven countries had been notified ahead of the opening date, covering equipment (including measuring instruments) fundamental studies of chemical kinetics, applied investigations and the germ of ideas about production. The British contribution of six papers included one devoted solely to studies of chemical production using fission fragments. In many countries considerable attention has evidently been paid to the field of polymerisation—modifying the properties of polymers by ionizing radiation, production of polymers, of grafts and co-polymers. Perhaps it is a bit early to expect realistic cost-studies but only two papers were explicitly devoted to this subject. Incidentally, a survey earlier in the year in *Khimicheskaya Promyshlennost*, 1959, No. 2, p. 99, by M. A. PROSKURNIN did discuss this among other industrial aspects for a number of reactions. Success in these lines of work would happily convert the sources of an embarrassing disposal problem into new productive assets.

Submerged Fermenter Scale-up

THE most important factor in scaling up unstirred tower type fermenters for the production of citric acid by the deep fermentation of beet sugar molasses is the aeration of the fermenter contents. However, despite the published large volume of work on mass transfer the available information is not sufficient to permit prediction of mass transfer for the type of bubble making devices used in fermenters. Moreover, mass transfer data for the bubbles produced by sintered discs is very scanty, the gas rates covered in most of the published work are greater than those of interest in fermentation, and most of the work on fermentation deals with relatively short, mechanically agitated vessels rather than unstirred columns.

D. MURPHY* and others have gone some way towards filling these gaps with a recent investigation. They set out to find the effect of such factors as gas flow rate, disc area and porosity, column diameter and height, oxygen partial pressure, and antifoam agents on the rate of oxygen absorption in copper-catalysed solutions of sodium sulphite. To elucidate the mass transfer performance they used two experimental columns, one 6 cm and the other 15 cm in diameter. In these, porous glass discs with three grades of maximum pore size 77.4, 12.2 and 5.4 microns respectively were used.

The work shows that the coefficient of oxygen transfer from the air to the sulphite increases with gas flow up to "flooding," a point characterised by coalescence of the bubbles and intense turbulence of the liquid. This coefficient decreases with increase in air pressure, and increases with decrease in disc pore size. It is adversely affected by surface active agents and it decreases markedly as tower diameter increases.

The fact that values of the coefficient as high as 140 gm/l. hr. atm. were obtained compared with figures of 50–60 for agitated vessels shows that a relatively high degree of aeration can be provided by deep towers. The authors, however, are in some doubt as to whether the required degree of aeration can be obtained in commercial equipment without the use of baffles and mechanical agitation, as well as the elimination of antifoam agents.

*D. Murphy, D. S. Clark, C. P. Lentz, *Can. Journ. Chem. Eng.* 1959. 37, 4, 157.

Characteristics of Bursting Discs

THE design of safety diaphragms, a subject of considerable controversy and difficulty, moves forward a stage through a recent contribution to the problem by N. A. WEIL.*

In discussing how the bursting pressure of a frangible membrane can be determined, he points out that the experimental approach does not offer safe predictions for conditions differing from those of the experimental, and that exciting theories are either too approximate or too cumbersome to provide an answer.

To remedy the situation, Weil has put forward a theory in which it is assumed that the true stress in a material in uniaxial tension can be represented by the product of its hardness factor and its logarithmic strain raised to the power "m," the strain hardening exponent. From this the bursting pressure can be determined.

He rejects the conception of uniform stresses and strains within the disc during deformation and at any pressure level, as being too crude to be useful. Instead he assumes that during deformation the particles of the disc material travel along paths which are arcs of a set of coaxial circles, and develops equations for estimating the polar deflection of a disc and its strain at instability.

From the evidence of disc behaviour assembled in this work Weil advises the use of materials with high values of the strain hardening exponents if a large deflection prior to bursting is desired. On the other hand if the desideratum is a high bursting pressure then a material with a high hardness factor should be used regardless of its strain hardening exponent.

Contrary to opinions which have been held on this aspect of bursting discs, neither purity of the disc material nor its annealed condition give adequate insurance of reliability of a disc in service.

The fact is that the reproducibility of bursting pressures depends only on the ability of the metal to stretch until the bulge passes through instability. This requires that in the uniaxial test the logarithmic strain at failure should exceed (0.36 + 0.73 m), in the bulge test the recorded pressure should pass through a maximum prior to bursting. Many pure metals, specifically certain grades of aluminium alloys, do not possess this ability.

A further word of caution is given. Regardless of the straining capacity of materials, premature fractures are more likely to occur if the material is very thin (if the material thickness is less than 0.020 in.). Therefore, if reliability of safety diaphragms is to be insured, this should not be obtained at the expense of material thickness, but rather by increasing the diameter of the disc.

* *Paper No. 59-APMW-3 presented at the West Coast Conference of the Applied Mechanics Division of the ASME. Sept. 9-11, 1959.*

The Future of the Fuel Cell

THE idea of converting a high proportion of the total free energy change of chemical reaction into electrical energy by an electrochemical device, an old idea first conceived by SIR WILLIAM GROVES in 1839, has encountered many impediments to its development. Such a device or fuel cell, to give it its proper name, was made to work at the turn of the nineteenth century, but the state of technology at that time, including means of control, and the lack of suitable materials of construction, prevented its further development.

But judging from the recent demonstration of the medium temperature fuel cell of Bacon, a project carried out under the sponsorship of the National Research Development Corporation it is clear that the time is not far off when the fuel cell will become a commercial proposition. And in this country, apart from the N.R.D.C., Sondes Place and others are also carrying out intense development work upon a high temperature fuel cell.

Bacon's cell, which uses hydrogen as fuel and oxygen as its oxidant, has an output of 5 kW at 24 volt on maximum load which represents an efficiency in the range 50-60%. One interesting application has been advanced by its sponsors, namely its use as an electrical accumulator when the national grid is operating at less than optimum load. The surplus power could be used for electrolysis to feed oxygen and hydrogen to a cell which would then be available as an auxiliary source of power. Among the advantages of medium temperature type of cell are its ability to take overloads at reduced efficiency without damage, its silent operation, and absence of effluents.

Objections have been raised against it on the grounds that the cost of fuel plus oxidant is already greater than the cost of power generated by more conventional methods even when these are carried out on a small scale. How valid this objection will be when tonnage hydrogen becomes a reality remains to be seen.

It seems certain, however, that under present-day conditions the use of a relatively impure gas for fuel, such as water gas, air as an oxidant and atmospheric operation, are all necessary before the medium temperature fuel cell can become a competitive source of power.

The high temperature fuel cell on the other hand has greater promise since it can use a cheap fuel and achieve a higher over-all electrical efficiency from the original fuel than possible otherwise. This requires the integration of the cell operation with the process producing the fuel gas, a condition which would lead to efficiencies approaching 80 per cent.

At present the largest single factor limiting power ouput from a cell is the high internal resistance and to be competitive with other methods of power generation, the resistances that have so far been reported for high temperature cells need to be reduced by a factor of 4-5.

How such an improvement can be brought about is discussed appropriately enough in a recent issue of a contemporary chemical engineering journal.* It is significant that one solution is seen to be the adoption of electrodes similar to those used by Bacon, which are pressurised double porosity electrodes. Such electrodes are known to be under development and if expectations are realised their internal resistance will be close to 1 ohm per sq. cm. as required for a current output of 200 amps per sq. ft. at 0.75 volt.

* *E. Gorin & H. L. Recht. Chem. Eng. Prog. 55, 8, 51.*

Performance of a Wiped Film Evaporator

THE interest in mechanical means of improving heat transfer rates continues to be well sustained as a number of recent reports show. Last month we mentioned the work of Lustenader and others which was described at a recent ASME meeting; following closely upon this work is an account from Germany of results obtained with a Luwa wiped-film evaporator* with water as the evaporated medium and steam as the heating medium.

The evaporator had a wiped film cylinder of about 6 cms in diameter and 49 cms in length, giving a swept area of approximately 0.1 m^2; rotor speed varied from 1010 to 2120 rpm. Boiling temperatures were in the range 30 to 90°C and steam temperatures were variable within the range of 50 to 150°C.

The conclusions drawn from some 200 experiments show that an average figure for the overall heat transfer coefficient is about 2120 Kcal/m^2 hr °C. Nucleate boiling plays an important part in the evaporation but at low Reynolds Numbers

film boiling comes more into the picture. At boiling temperatures of 50°C and above a high overall temperature difference leads to higher values of the overall coefficient. At a boiling point of 80°C and for a temperature difference of 20°C the coefficient had a value of about 2100. At the same boiling temperature a coefficient of 2530 was obtained for a temperature difference of 67°C.

Among the other factors influencing heat transfer rates increase in boiling temperature and greater rotor speed both tended to give higher rates of heat transference; increasing the rotor speed from 1010 to 2120 rpm gave a 10% increase in the overall coefficient. Increase in liquid loading was also shown to give higher heat transfer rates.

* *H. A. Leniger and J. Veldstra. Chem. Ing. Tech.* 1959, 31, 498.

Assessing Finned Tubes for Nuclear Boilers

FINNED surfaces are now often employed where the thermal resistance on the outside of a tube is much greater than that on the inside. For the detailed case of steam raising in boilers of nuclear power stations, EDISS, BILSBOROUGH and CARR have now published studies* comparing the performance of plain and finned tubing. Practical considerations of fin manufacture are taken into account in the assessment which includes production of a family of curves giving the relationship between fin thickness and fin height for various values of the outside film coefficient (h_o). Noteworthy is the figure giving results of an economic survey undertaken by the authors. This gives variation in the cost of generated electricity for ranges of fin height and number of fins per foot for selected values of h_o showing clearly the minimum cost regions. These costs are for the boilers only, not for the whole nuclear power station. For these conditions, minimum cost was obtained using a fin of height 0.06 ft, thickness 0.0055 ft. at a spacing of 40 fins per foot. The survey apparently took into account the cost of the pressure vessels, the price of extended surface and of fittings associated with the matrix. In costing the power consumption, only the pressure drop over the matrix was considered.

* *Nuclear Power, July*, 1959, *p.* 80, *August*, 1959, *p.* 95.

Flotation of Molybdenite from Copper

MOLYBDENUM is found in small amounts in practically all low grade porphoritic copper ores. It is usually present as the sulphide, molybdenite, which is readily recovered in the copper flotation concentrate. Copper sulphide flotation concentrates may contain from 0.25% to 1.00% MoS_2. When such ores are milled in large tonnages the amount of molybdenum present may be substantial. Consequently, nearly all major copper producers now have molybdenum recovery systems.

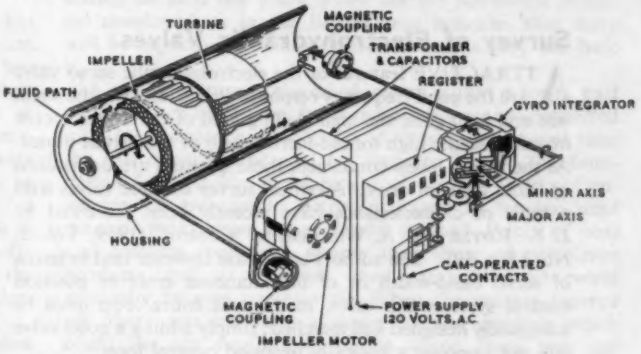
In the Denver company magazine *Deco Trefoil*, Vol. 23, No. 3, an interesting flowsheet study is given of a typical successful treatment system based entirely on reagent control and flotation to separate the molybdenite from a copper sulphide flotation concentrate. No heat treatment, steaming or roasting steps are used. In this process sodium ferrocyanide and sodium cyanide are used as copper mineral depressants while sulphuric acid is used to modify pH.

Main stages are copper-molybdenite flotation, molybdenite flotation then selection flotation cleaning of the "rougher" molybdenum concentrate. Before final cleaning the MoS_2 concentrate is reground in closed circuit with a pump and cyclone classifier. Water is added as required to maintain the classifier overflow at 8 to 10% solids, while the underflow returned to the regrind mill, contains about 70% solids. The cyclone overflow is cleaned five successive times by flotation to bring the MoS_2 up to final grade of plus 90%.

Direct Mass Flowmeter

LIQUID and gas flow can be directly measured in pounds by means of a "true mass" flowmeter jointly announced by General Electric and Black, Sivalls & Bryson Inc. Essentially the instrument consists of an impeller and a stationary turbine. The impeller, driven through a magnetic coupling at a constant speed by the synchronous motor, gives an angular momentum or twist to the fluid as it enters the instrument. The fixed turbine removes this momentum and receives a torque proportional to the mass rate of flow.

A magnetically coupled linkage transmits this torque to the gyro-integrating mechanism where it is applied around the minor axis of the gyroscope. This causes the gyro to rotate about its major axis at a rate proportional to the torque. This rotation is transferred through a gear train to the cyclometer register where the mass flow is integrated and indicated in pounds.



The complication of the gyro-integrating device is introduced apparently to permit operation from an unregulated power supply without any measurable effect on meter accuracy. The gyro motor and impeller motor run synchronously and operate from a common power supply. Thus nominal line-frequency fluctuations (plus or minus 5%) will affect their speed to exactly the same extent and the gyro precession rate will still be in exact proportion to the mass flow rate. Fluid temperature range is given as 0°F to 165°F with flow rates up to 40,000 lbs./hour for gases or 240,000 lbs./hour for liquids.

Where There is Smoke

IN assessing smoke from fire what properties should be measured? Possibly the most important are the chemical composition and hence toxicity, particle size distribution and hence effect on the obscuration of sunlight, height of discharge and temperature of the flue gases. There are also others. However, the effect of the smoke as a pollutant will usually be significantly related to a single parameter—the weight of smoke emitted. Yet for certain administrative purposes industrial smoke is assessed by optical methods. Is this justified for such smokes and for those from domestic fires?

A critical—theoretical and practical—examination of this subject by R. DICKINSON and colleagues* has led to the conclusion that there is no fixed relation between smoke concentration and optical density; the ratio R of the true weight of smoke to that estimated from the optical method varies widely under different conditions.

A series of investigations showed that the main factors associated with changes in R were the average smoke concentration and the optical system of the smoke meter. Fuel bed conditions and agglomeration had little significant effect. Light scattering effects at high concentrations are the ultimate

reason for the unreliability of optical measurements. Work still in hand suggests that even at low concentrations further factors may operate which can give rise to large errors in estimating weight from optical density. Mr. Dickinson therefore considers that optical measurements have severe limitations when used to assess the weight of smoke in domestic flue gases. It is interesting to note that this receives some confirmation from earlier results on a Lanchashire boiler. Although at either full or half load on the boiler, a linear relation between optical density and smoke concentration was found, the constant of proportionality was considerably different at the two loads. Thus the optical smoke meter cannot be used until it has first been calibrated against a direct gravimetric measurement. However, since the optical smoke meter gives a continuous record, it gives a rough guide to the pattern of smoke emission and therefore fulfils a useful function.

* *Institution of Heating and Ventilating Engineers*, 1959, *Vol.* 27, *p.* 108.

Survey of Electrohydraulic Valves

ATTRACTIVE features of the electrohydraulic servo valve are the good frequency response characteristics, the small size and high gain, the high stalling load of the driven motor or ram and the high torque-inertia ratio of the driven motor. At the power levels concerned, these qualities are unmatched by other types of drive. A critical survey of these valves with a table of characteristics have recently been presented by J. K. ROYLE and A. WILLIAMS in "Control" (1959, Vol. 2, No. 14, p. 89). The authors emphasise however that in terms of servo band-width or of instantaneous error of position control systems the valve, motor and entire loop must be adequately designed and matched; simply adding a good valve will not improve a basically unsound control loop.

Examples are given in the table of seven series of electrohydraulic valves made in Britain and now available. They cover a wide range of flows and employ three types of torque motors. The Moog valve uses a flapper operating between two jets of fluid. The flapper is displaced by the force developed between the two coils of the torque motor and the hydraulic, magnetic and elastic forces are adjusted to give a hydraulic pressure output proportional to electrical input. A further type is based on an oscillating diaphragm, again between two jets of fluid. The diaphragm follows a square wave excitation at a particular frequency and flow is varied by adjusting the time of rest on one side or the other by varying the mark/space ratio of the square wave. Both of the above are used on valves with two hydraulic stages. The Laws relay, however, relies on the rotation of a shaft between the coils and can be used to move a spool directly. It is therefore suitable for controlling flow in valves with either single or double hydraulic stages.

Natural Rubber Fights Back

TO meet the challenge of synthetics, the natural rubber industry is going ahead with a vigorous replanting programme and planning intensified research. In Britain, the non-profit-making body Rubber Technical Developments Ltd. is responsible for development work at the pilot-scale and production stages. The latest annual report shows a programme which includes juggling with techniques of depolymerising natural rubbers and reinforcing with synthetic polymers. Aim of the work is to produce a fluid compound which after casting to shape can be polymerised and vulcanised to a strong, solid, elastic mass. Previous work had shown the possibilities of the use of depolymerised rubber and styrene to obtain such a compound. Normal vulcanisation agents interfere with the polymerisation of the styrene and it is therefore necessary to use a peroxide vulcanisation system. With this system, thin section vulcanisates can be successfully produced with reasonable physical properties at hardness values of 60° B.S.I. and above. Softer vulcanisates necessitate reducing the styrene content which in turn calls for a lower viscosity depolymerised rubber in order to obtain the required fluidity. These products have poorer physical properties. As the size of the mass is increased the internal heat generated during reaction becomes greater and polymerisation at lower temperature is essential to obviate large temperature inhomogeneity. However, as the temperature is lowered, the polymerisation periods must be lengthened and this becomes excessive with large masses—the outlet for which the casting technique is most attractive. For the moment, it appears that this ingenious approach is best suited for thin section mouldings although it may have wider potentialities if temperature control can be improved.

Lessons of an Oil Refinery Fire

AN account of a major fire at a Californian oil refinery last year has been quoted by the F.P.A. Journal (July, 1959) with an important list of observations. Apparently, a wave of burning oil froth swept over 27 acres of a 33-acre site causing the death of two employees, minor injury to 18 fire-fighters and extensive or total destruction to 13 out of 40 major tanks. Loss was estimated at nine million dollars.

After the holocaust, what where the features observed? (1) Unprotected steel supports failed but protected ones remained comparatively undamaged. (2) Pipe insulation tied with iron wire behaved well but metallic binder-straps failed. (3) All welded steel piping with provision for expansion withstood the effects of fire but most of the cast-iron fittings, large screwed pipe couplings and screwed valves failed. (4) Wired glass in the windows of the control rooms melted allowing the fire to enter and destroy a great deal of costly equipment. (5) Brass fittings on the plant fire main melted and could not be used until replaced. (6) Hydrants in or near drainage ditches were not accessible during the fire in its early stages. (7) Open drainage ditches presented a severe fire hazard when burning oil flowed through them.

Gasket Sealing Pressures

THE problem of finding the maximum variable pressure which may be sealed within a pressure vessel by a bolted gasketted joint does not appear to have received a great deal of attention from the literature until recently. To find this pressure it is necessary to find the gasket reaction in a pressure condition, a matter of some difficulty because the applied pressure changes the relation between the gasket load and the bolt load. Actually three kinds of gasket reaction may occur, elastic when the gasket material is not stressed beyond its elastic limits, plastic when the material is overstressed, and springy when the gasket is fully enclosed.

Plastic reaction is not of much use in a vessel subjected to varying pressure for releasing the internal pressure increases the crushing of the gasket, which will leak when high pressure is again applied to the vessel interior.

By analysing the system of forces arising from the internal pressure within a vessel, the bolt load, and the gasket reaction, G. P. KOTELEWSKY* has developed a method for estimating the maximum sealing pressure which a joint can tolerate. The method is represented by a simple equation which its author applies to a practical problem. In addition he presents a table of maximum sealing pressures results calculated for a standard 24 in. flanged connection and compares the results calculated by the equation for flanged joints with those calculated for a high pressure closure, the Multilok which will withstand a pressure three times greater than will a conventional flanged joint.

* *Ind. Eng. Chem.* 1959, 51, 8, 949.

British Chemical Engineering
A HEYWOOD PUBLICATION

Petroleum Chemicals Thriving

WHAT are the limits to the phenomenal current expansion of petroleum chemicals manufacture and when are they likely to be reached? By 1958, this essentially post-war branch of the chemical industry was estimated to be producing 40% by value of British chemicals and consuming about 1,300,000 tons of "raw materials" taken from the oil industry.

Both the proportion and absolute amount involved are rising rapidly. We recently visited the third olefin plant of I.C.I. Heavy Organic Chemicals Division, which has been successfully brought into operation at Wilton. It is based on light naphtha and will raise the production of ethylene by I.C.I. alone to about 110,000 tons a year, with the possibility of increasing this figure by relatively minor modifications of plant to 140,000 tons. This may be compared with the total output of ethylene in Britain for 1958 of 230,000 tons. About 90% of the ethylene made in the three plants at Wilton is being used for making polythene at neighbouring plants, the remainder going for the manufacture of ethylene oxide at present by the chlorhydrin method, but later by a direct oxidation process.

Pyrolysis is carried out by the steam-cracking process of Kellogg. The first olefin plant on the site, commissioned in 1951, was considered a pioneer showpiece and has now been copied by all the major oil companies. A major asset is its freedom from coking, offsetting the higher capital investment where rising demand and interdependence with other plants place a premium on continuous operation over long periods. Decisions to construct two further plants in turn, based on essentially the same method, are a tribute to the satisfactory results gained with the first plant. Now that the third unit has been brought on stream, this complex is said to form "the largest petroleum chemical venture outside the U.S. and the largest anywhere based on liquid feedstock". The distinction between these two claims arises from the fact that U.S. plants are characteristically based on gas feeds—refinery tail gases or natural gas.

Primary products of the new olefin plant are ethylene and propylene of high purity, methane, ethane, hydrogen, butylenes and butadiene, high-octane gasoline and fuel oil. Apart from the last two, these are used as intermediates for making products ranging from hydrogen cyanide for acrylic fibres through synthetic rubbers to ethylene oxide, serving as a starting point for a very wide range of end-products. But there can be little doubt that a dominating role in the decision to go forward with this project was played by the striking rate of expansion of demand for plastics; ethylene is considered the chief product and propylene the next most important. It may be recalled that Mr. S. P. Chambers, now chairman-elect of I.C.I., drew attention to the rising role of plastics in the chemical trade during a lecture last March to the Plastics Institute. Mr. Chambers noted that world exports of plastics in 1957 were more than three times those in 1952, although the figure for total chemicals on the same basis in that year was 175%; we could draw comfort from the fact that plastics—the expanding group—formed a larger proportion of Britain's chemical exports than it did for the world as a whole, namely 12.8% compared with 11.1% in 1957. This happy relation was also true of Britain's exports to Europe. For chemicals as a whole we accounted for 10.7% of Europe's imports in 1956; for plastics the figure was 15.9%. The announcement that his company intend to develop, during the next few years, a new site for petroleum chemical developments in the Bristol area indicates that there will be no resting on these laurels as far as they can help it.

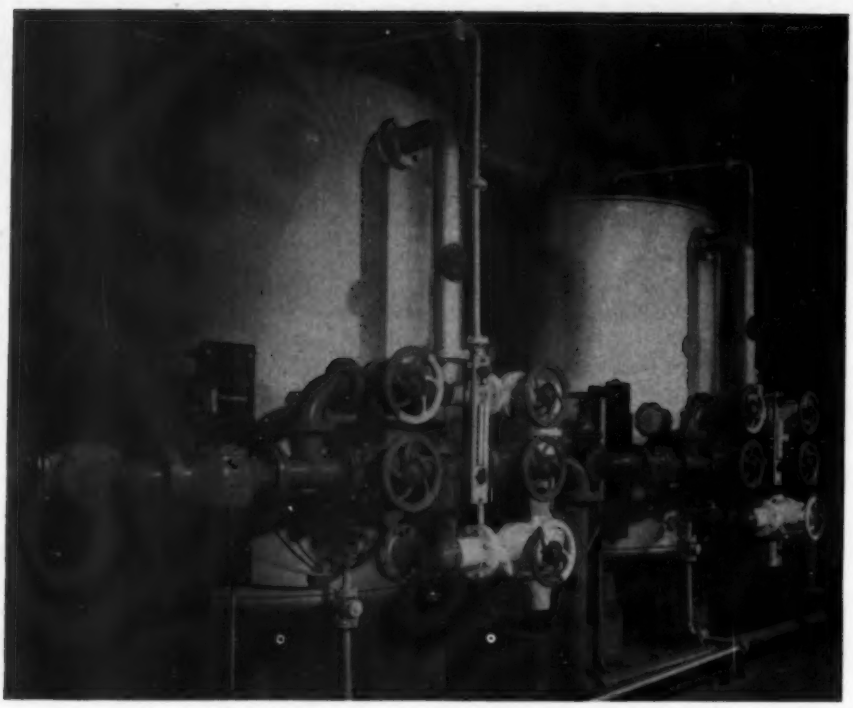
A sadder feature of the development is that it forms part of the switch of interest from indigenous coal to imported oil. The experience gained in coal hydrogenation and later the hydrogenation of coal tar creosote formed the foundation for post-war development of the Oil Works. Conversion of creosote to petrol managed to survive until August, 1958, when it was finally stopped. Prices of coal and creosote rose more steeply than those of petroleum products and, as a result, their conversion to petrol gradually became uneconomic. When the process tapered off, there was naturally a desire to find projects which could use the equipment. In the event, there was not enough space at Billingham to provide for the post-war developments planned partly as a result of this, and the Olefine Works was therefore set up at Wilton.

Brief reference has been made above to the products of this latest plant, other than ethylene and propylene for polymerisation. Most of the ethylene oxide is converted to ethylene glycol, which is then used for making Terylene and explosives, apart from its sale as an anti-freeze agent and for further applications by other divisions (making detergents) and other manufacturers. From propylene will be made propylene oxide and propylene glycol. Across the River Tees in the inter-linked Oil Works propylene is converted to the azeotrope of isopropanol and water—part of this being used to form acetone, part refined to pure isopropanol. In a carbonylation plant, some of the propylene is converted by a modification of the German OXO process by the addition of carbon monoxide and hydrogen to give normal and iso-butanols, sold as solvents and solvent intermediates. In this plant, incidentally, higher olefins supplied by the oil companies are also converted to the corresponding higher alcohols. The principal outlet for these is for the manufacture of phthalate plasticisers in polyvinyl chloride compositions.

Butenes separated from the mixed C4/C5 stream go to a number of units, known collectively as the alkylation plant, to be reacted with phenols and cresols yielding antioxidants for petrol, transformer oils and foodstuffs. Here again there are plans for extending the range of products—in this case, alkylated phenols.

This gives a skeleton outline of the process routes and products. What of the plant? In our following issue we hope to give further information about this impressive construction now making a major contribution to an industry which is effectively no more than ten years old—infant in years, giant in achievement.

66.094.94



The illustration left shows a two-bed demineralisation plant.

PRINCIPLES AND PRACTICE OF ION EXCHANGE

A technique for the concentration of valuable materials and the recovery of industrial wastes

by T. R. E. KRESSMAN, Ph.D., D.I.C., F.R.I.C.

ALTHOUGH the phenomenon of ion exchange was first observed about 100 years ago and the principle has been used industrially since the beginning of the present century, the considerable advances that have occurred in the field in recent years can be attributed directly to the existence of the ion-exchange resins, first synthesised by ADAMS and HOLMES in 1935.[1] Most of the modern resins, with their high stability and ion exchange capacity, are based on polystyrene and are broadly of two types: those capable of exchanging cations and those capable of exchanging anions. The cation exchangers may contain COOH groups and be weakly acidic, or SO_3H groups and be strongly acidic. The anion exchangers may contain primary, secondary or tertiary amino groups, resulting in weakly basic properties, or quaternary ammonium groups which confer strongly basic properties on the materials.

The strongly acidic material is the more commonly used cation exchanger and will exchange all the ions in a solution for another ion, including the hydrogen ion. The weekly acidic material is used for exchanging cations associated with the anions of weak acids, generally at *p*H values above about 8. The weakly basic anion exchangers are used for ordinary demineralisation and for the absorption of strong acids. They have only a low capacity for weak acids like acetic acid. The strongly basic exchangers have a high capacity not only for the strong and ordinary weak acids, but will also take up such feeble acids as silica, CO_2, phenols, HCN, etc. They are used in large quantities for removing silica and CO_2 from water and for exchanging anions in neutral solution just as the strongly acidic resins are used for exchanging cations:

$$R.NO_3' + KCl \longrightarrow R.Cl' + KNO_3$$

compare

$$R.Na^+ + KCl \longrightarrow R.K^+ + NaCl$$

The resins will exchange not only simple ions but complex ions also. Some complex ions are stable only under

Dr. Kressman *is Chief Research Chemist to The Permutit Co. Ltd., and has worked in the field of ion exchange for nearly 20 years, originally under B. A. Adams. He is co-author (with C. Salmon) of "Ion Exchangers in Organic and Biochemistry" and many patents and original papers have appeared under his name.*

certain conditions of concentration and *p*H, and this fact can be exploited to separate or to remove them. For example, the iron that is present in commercial concentrated HCl exists there as the anion $FeCl_4'$. In dilute acid solution, however, or in water, the complex decomposes to give cationic iron. A method for purifying commercial HCl uses this principle.[3] The impure acid is flowed through a column of an anion exchanger in the chloride form: the iron is taken up as the complex anion and the acid emerges iron-free. When the column is saturated with iron it is regenerated for further use merely by flushing with water: the $FeCl_4'$ decomposes to chloride, which remains on the resin, and $FeCl_3$, which appears in the effluent. The resin is then ready to treat a further quantity of acid.

Complexes do not need to be present in the solution, but can be formed actually at the exchanger sites. An important example is the formation of the $UO_2(SO_4)_3''''$ ion from a resin sulphate and UO_2SO_4 solution, a principle which is used in the recovery of uranium from its ores[3]:

$$2\ Resin_2SO_4 + UO_2SO_4 \longrightarrow Resin_4UO_2(SO_4)_3''''$$

The uranium ore is leached with sulphuric acid, filtered, and the *p*H of the filtrate adjusted to about 1.8. The solution is then flowed through a column of anion-exchange resin until the resin is saturated with uranium, when it is eluted with a slightly acid salt solution to yield the uranium in comparatively concentrated solution. Since iron is the only other metal with which the uranium is associated that forms anionic complexes under these conditions, the process is nearly specific for uranium and a very pure uranium solution is obtained. Apart from water treatment, this is the largest single application of ion exchange. Indeed, without ion exchange the recovery of uranium from the many low-grade ores in which it occurs would be almost impossible. Ion exchange is thus an indispensable adjunct to the winning of uranium and many extremely large installations are in use in South Africa, Canada, Australia and elsewhere.[4] A typical installation is shown in Fig. 2. This is fully automatic and the electrical and hydraulic gear that controls the cyclic operations is housed in the cabinets shown in Fig. 1.

The success of the uranium process has prompted a study of ion exchange for the recovery of other metals, notably gold.[5] However, although this has been technically successful the economics, when compared with those of the existing process, are doubtful.

Ion-exchange reactions are mostly carried out in aqueous solution. However, exchange will occur in the presence of non-aqueous solvents, provided, of course, that the species to be exchanged do exist in the solvent as ions. That is to say, there must be an ionising solvent in the system. Aqueous alcohol and aqueous acetone solutions present no problem, the exchange occurring nearly as rapidly with 60 or 70% organic solvent as in pure water. The exchange of ions in completely non-aqueous solvents can be performed by making sure the resin contains its own gel water—the water that swells the resin and is within its gel structure. This water is tightly held to the resin and has no tendency to come out and contaminate the non-aqueous solvent being dealt with, but at the same time it provides an ionising environment at the resin-solvent interface in which the exchange can occur. Examples are the removal of Cu^{++} from methacrylic acid, to which it is added as a polymerisation inhibitor, with the aid of a cation exchanger, and the removal of acetic acid from benzene and of hydroquinone from styrene, both with an anion exchanger.

Methods of Use

(a) Batch Method

The simplest method of carrying out ion exchange is merely to agitate the exchanger with the solution to be treated and then to separate the resin and solution with the aid of a coarse filter. If the simple exchange of ions is to be performed, this is not generally a very efficient method unless the ion to be removed from the solution has a high affinity for the resin, because ion exchange is always an equilibrium process and, in consequence, will never go to completion in a stirred system, e.g.:

$$Resin\text{-}H + Na^+ \rightleftharpoons Resin\text{-}Na + H^+$$

The exchange of sodium for hydrogen can be induced to proceed further by removing the resin from the solution (say, with the aid of a screen) and adding fresh resin. In principle, this can be repeated as often as desired. The method is not often used, as it is tedious and costly, but there are occasions when it is the only practicable one as, for example, when the solution being treated is too viscous to flow through the more conventional column of resin, or if the solution contains much suspended matter. It has been used in the extraction of pectin from grapefruit peel, the cations being exchanged for hydrogen ions by stirring the peel with water and a cation exchanger prior to centrifuging and concentrating the pectin solution.[6]

If demineralisation is to be practised, both a cation- and an anion-exchange resin will have to be used and the process is then somewhat more efficient, especially if a strongly basic anion-exchanger is used, because the anion-exchanger disturbs the equilibrium and allows the reactions to proceed to completion

$$R.H^+ + NaCl \rightleftharpoons R.Na^+ + HCl$$
$$R.OH' + HCl \rightleftharpoons R.Cl' + H_2O$$

The second equilibrium lies so far to the right that it goes virtually to completion.

(b) Column Method

The most common method of carrying out ion exchange is with a column. In the simple case where one ion is to be exchanged for another, a single column is used. For demineralisation two units running in series are employed, or a single column containing a mixed bed can be used. Except for the mixed-bed unit, to be described below, the design of the units is substantially similar. If acid solutions are being handled, as in demineralising, the mild-steel shells and pipework must be suitably protected and almost invariably rubber lining is employed. The diameter of the unit may be between 6 in. and 12 ft, depending on the size of the installation. Irrespective of the size, it is desirable that the bed or column of resin should have a height of between 4 ft and 6 ft and a rising space equal to about 50% of the bed height be allowed above the bed. In this rising space the resin can expand when it is backwashed, an operation that is carried out after each run in order to loosen the bed and to remove any air bubbles and suspended matter. Thus the cylinder will be between about 6 ft and 9 or 10 ft on the straight, the top and bottom being dished. The bottom contains a supporting medium—frequently graded gravel—for the resin, and a collecting system for the water or other liquid being treated. The ion-exchange material is in the form of particles −14+52 mesh, consisting of either granules or small spheres.

Both running and regeneration are almost invariably downflow. On paper the ideal would be a countercurrent flow system with the regeneration, say, upwards and the run downwards, because in this way the maximum regeneration is achieved at that end of the resin column which is the outlet in the running cycle. In practice, however, unless adequate precautions are taken to avoid disturbance of the bed during upward flow, chanelling occurs and results in a performance inferior to that with concurrent downward flow.

The rate of liquid flow through the column during a run is generally of the order of 8 gal./sq. ft min., although if large ions are being exchanged (and the rate of exchange

Fig. 1. Control Equipment for the Buffelsfontein Uranium Plant

Fig. 2. Ion Exchange Plant for Uranium recovery at Buffelsfontein, S. A.

is consequently slow), or if rather viscous or concentrated solutions are being treated, flow rates as low as 1 or 2 gal./sq. ft min. may be used. The regenerant solution is passed through the column during about ¼ hr and this is followed by a water rinse to remove excess regenerant prior to the next run.

The quantity of regenerant used in practice is invariably less than that required to regenerate the resin fully. This is a matter of economics, since the higher the degree of conversion of the resin the greater is the amount of regenerant required to produce a further conversion. In general a resin will be regenerated to about one-third or one-half of its theoretical maximum capacity, and something like 1.5 bed volumes (9.5 gal./cu. ft) of 10% sodium chloride solution, for example, will be used for regenerating a sulphonated polystyrene resin like Zeo-Karb 225 in the sodium cycle.

In commercial installations the regenerant is introduced into the unit from the regenerant tank with the aid of an ordinary Venturi type of injector powered by mains water. This also serves to dilute the somewhat concentrated regenerant solution so that it enters the unit at the correct strength.

Frequently ion-exchange is used as a concentrating step, the object being to obtain an ion, present originally in a dilute solution, in as concentrated a form as possible. This is done by taking up the ion on to the appropriate resin and then using a concentrated eluting or regenerant solution. An example of this is in the treatment of industrial effluents where a valuable or noxious ion is required in a small bulk of solution, either for working up or for disposal. In the metal finishing industry chromic acid occurs in certain rinse waters in concentrations of 100 to 200 ppm, and by taking this up on an anion-exchange resin and subsequently eluting in stages with 7.5% caustic soda solution, a 15% solution of sodium chromate is readily obtained. This represents a concentration of something like 1000-fold and the disposal of the chromate becomes a practical proposition.

The eluting in stages (or split regeneration) can be understood from Fig. 3, which is a typical curve relating the concentration, in the regenerant effluent, of the ion being eluted with the volume of the effluent. If the effluent is collected in one lot the concentration of the ion in the bulk will be the area under the curve divided by the volume of the effluent. In the split regeneration technique the effluent is collected in three fractions represented by the two vertical lines. The middle fraction clearly contains the ion in high concentration and this is kept as product. The two fractions to the left and right of the vertical lines are bulked and used, after the addition of pure regenerant chemical, for the first part of the next regeneration, this being followed by a further volume of fresh regenerant solution equal to the volume of the previous middle fraction.

Loadings of the columns can be increased by using several of them in series, and, when the ion in question breaks through the first one, the solution is fed to the next one. When the ion breaks through this one a third column is introduced at the end, the flow being continued through the second and third. Simultaneously, the first column is removed from the circuit and regenerated, the split regeneration technique being used if high concentrations of the ion are required. When the third column breaks through, the second is taken out of circuit for regeneration and the regenerated first column is put on to the end of the third. This cycle can be continued indefinitely and assures the columns being loaded to virtually 100% of their capacity.

This method is used for the recovery of uranium, already referred to. It has the further advantage here, where a valuable product is being dealt with, that no loss of uranium occurs as there is no leakage from the columns.

(c) Mixed-bed Column Method

In 1941 it was discovered that a column of an intimate mixture of previously regenerated cation- and anion-exchange resins gave a higher degree of electrolyte removal than did the two-bed system, and the product, in consequence, contained a lower residual electrolyte content.[7] This enhanced purity is obtained because the mixed bed of resins represents, in effect, very many consecutive cation- and anion-exchanger pairs, so that any drop of solution being treated is subjected to the demineralising action many times over. Furthermore, anything—organic or inorganic—coming from the one kind of resin is taken up by the other. An additional advantage is that only one cylinder is required in place of the two that are required when the two resins are arranged separately.

These advantages could not be exploited because no means could be devised of regenerating the mixture when it was exhausted and it was uneconomic to discard the exhausted unit. It was impossible, by the use of conventional regenerants, to regenerate the resins while they were mixed together, although several novel methods were studied in an attempt to do this, all of them unsuccessfully.

Such was the position until 1948, when it was observed that a cation-exchanger of the polystyrene type had a bulk

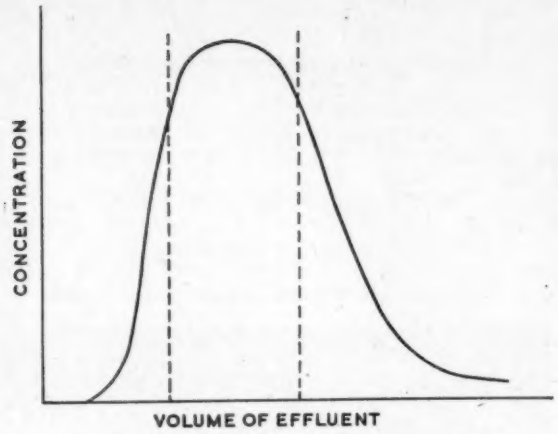


Fig. 3. Regenerant-Effluent Concentration Curve.

density appreciably greater than that of the corresponding anion-exchanger, and this immediately suggested a method of separation prior to regeneration. On subsequent remixing the resin would be ready for another run.

The method adopted, and still the method used today, is as follows. The cylinder containing the resins is similar to that used in ordinary two-bed ion exchange, but in addition to the distributor at the top and the collecting system at the bottom there is an intermediate collecting system arranged at the interface of the two resins when they are lying separated in the column. The anion-exchange resin is regenerated by introducing alkali through the top distributor and taking it off at the middle collector, following it with a quantity of water to remove the excess alkali. Likewise, the cation-exchange resin is regenerated by introducing acid at the middle collector and taking it off at the bottom one, this also being followed by a water rinse. The two resins are now mixed by passing in a stream of air through the bottom collector, from where it passes up through the column of resin and out at the top of the cylinder. The mixed bed is allowed to settle and the water to be treated flowed in at the top of the unit and out at the bottom as normally.

When the unit is exhausted a stream of water is passed upwards through the column at a rate sufficient to fluidise the whole bed. The constituents of the mixture separate according to their densities, and after 5 or 10 min. the flow is stopped and the bed allowed to settle. The heavier cation material will be lying at the bottom and the lighter anion at the top. Regeneration is then carried out as before

Typical Mixed-bed Plant

Fig. 4 shows a typical mixed-bed plant. Externally it appears similar to any other ion-exchange plant except, of course, for the valves and interconnecting pipework, all of which are associated with the single cylinder rather than with two cylinders as with a two-bed demineraliser. Internally, the main differences are the presence of the middle distributor and the different collecting system at the bottom. Gravel is not satisfactory for this collector and a specially designed system of lateral feeders is used.

By the use of a mixed bed containing a strongly basic anion-exchange resin, the solids content of, say, tap water can be reduced to a level at which the individual ions are completely unmeasurable. The total dissolved solids content is appreciably less than 1 ppm, corresponding to specific conductivities of the order of 0.1 to 0.2×10^{-6} reciprocal ohms.

Membrane Electrodialysis Cells

Partly for mechanical and partly for economic reasons conventional ion-exchange resins, even the modern high-capacity polystyrene materials, cannot be used for treating solutions of concentration greater than about 1%. This has set a limit to conventional materials, but the use of ion-exchange resin membranes arranged in an electrodialysis cell has enabled this concentration barrier to be broken.[8] These membranes have all the properties of conventional ion-exchange materials, but are in extended sheet form instead of the usual granular or bead form. A membrane or barrier having cation-exchange properties will readily permit the passage of all cations while largely preventing the passage of anions and, likewise, an anion-exchange barrier will readily permit the passage of all anions but will oppose the passage of cations.

The membrane cell consists of alternating cation- and anion-selective membranes, a cell normally containing some 300 or more, the spaces between them forming the alternate desalting and concentrating compartments. The cell is bounded by electrodes to which a potential is applied. The passage of the electric current results in the salt being concentrated in alternate compartments and depleted in the remaining compartments. The cell may thus be used either as a demineralising cell, the product being the demineralised solution from the one set of compartments, or as a concentrating cell, the product then being the concentrated solution from the other set.

For economic reasons demineralisation is not continued to levels below about 500 or 600 ppm, since the electrical resistance, and hence the power consumption, becomes excessive. This level of solids, however, represents a perfectly potable water and can be produced from brackish waters containing up to 30,000 ppm or more of solids, although it is doubtful if it is economic at present to treat waters containing more than about 10,000 ppm solids.

Membrane Process Costs Speculative

The costs of the membrane process are somewhat speculative at present. The power cost can readily be obtained from the power consumption (in kilowatt-hours per 1000 gal.) and the cost of electricity per unit. Typical figures for power consumption are given in Table 1, although it must be realised that these will depend on the current density used. The higher the current density, the higher will be the power requirement but the smaller the plant for a given job. In this country electricity would be costed at about 1d. per unit, but elsewhere in the world it might well be many times higher. Depreciation, maintenance and replacement costs cannot be accurately computed at present, particularly as they depend so much on the design of the plant and on the membranes. However, an indication of the order of magnitude of these items may be gained from the costings of a large plant now being installed in South Africa, which suggest that the costs are equally divided between depreciation, power and maintenance, each comprising one-third of the total.[9]

Although the process has been primarily developed for the desalting of brackish water, it is, in principle, applicable to the desalting of other solutions. In particular it has been studied for desalting sugar and amino-acid solutions, although these have been small-scale experiments only. As with water treatment the economic lower limit for the residual salt content is about 500 ppm; if complete desalting is required this effluent can be fed to a conventional ion-exchange plant which will deliver large volumes of completely demineralised solution from an influent of this concentration. In the same way, of course, completely demineralised water may be produced from brackish water although this is rarely necessary, it being generally sufficient to produce a potable water.

Continuous Ion Exchange

Conventional column ion exchange is essentially a batch process in that the unit must be shut down at intervals for regeneration. To obtain a continuous supply of treated solution from the plant two units are necessary, the one being regenerated while the other is running. This is, of course, a disadvantage, and one that can be avoided by a continuous process.

As is usual with a continuous process, the plant can be smaller than the batch plant and this can be well appreciated in the particular case of ion exchange by considering the batch plant illustrated diagrammatically in Fig. 5. The raw water flowing through the column progressively saturates it with ions and only a comparatively narrow zone is actually exchanging ions at any one moment. Depending on the equilibrium conditions, this exchange zone may be only a few inches high. The exchanger above it, saturated with the ion being removed from the water, serves only to obstruct the flow of solution, while the unreacted resin below has to deal only with already-treated water and thus takes no part in the process until the advancing front reaches it.

It is not feasible to dispense with the upper and lower portions of the column and make the height of the column equal to that of the exchange zone, since the unit then becomes uneconomically small and the cycle impractically short. However, it is feasible to move a quantity of resin corresponding more or less to the exchange zone through running, regenerating and washing zones in sequence within a column or a series of columns. The principle of continuous column ion-exchange of this sort is surprisingly old, a continuous ion-exchange softener having been described as far back as 1926.[10]

Various methods are used for moving the resin. In one a rotating plug valve transfers a fixed quantity of resin on each revolution from a regenerating and washing zone to an absorption zone.[11] In another, water passing through a venturi at the bottom of the column carries resin with it to the top,[12] while in a third a sequential timer operates a series of rotary valves in conjunction with a piston, the movement of which causes the resin to move.[13]

A continuous ion-exchange process working on a rather different principle consists of an endless hollow belt containing ion-exchange resin and tied every 6 in. or so, rather like a string of sausages. This belt is moved with the aid of rollers through regenerating, rinsing and running zones.[14] An extension of this uses an ion-exchange material, itself in the form of a continuous flat belt or band.[15]

At present only two types of continuous ion-exchange equipment have reached commercial production (in the U.S.A.), both of these working on the moving-column principle. It is not known how reliable these are, but it seems clear that more development work is required before continuous ion-exchange reaches the position of being a serious competitor to conventional column ion-exchange. Nevertheless, it will probably do so within the next few years.

Conclusion

Ion exchange as a unit operation is of wide and varied application. It performs a function that cannot be performed by any other operation in the purification of solutions in water treatment, the concentration of valuable materials and the recovery or concentration of waste materials.

For comparatively dilute solutions conventional column techniques are used, while for more concentrated solutions the electrodialysis method using ion-selective membranes is now becoming a practical proposition. The latter provides a continuous process for the treatment of brackish

TABLE 1—Power Required for Electrodialysis

Solids content ppm	Power—kWh per 1000 gal.
3,000	14
5,000	22
8,000	35
10,000	45
33,000 (sea water)	100

Fig. 4. A 30,000 gallon per hour mixed-bed demineraliser.

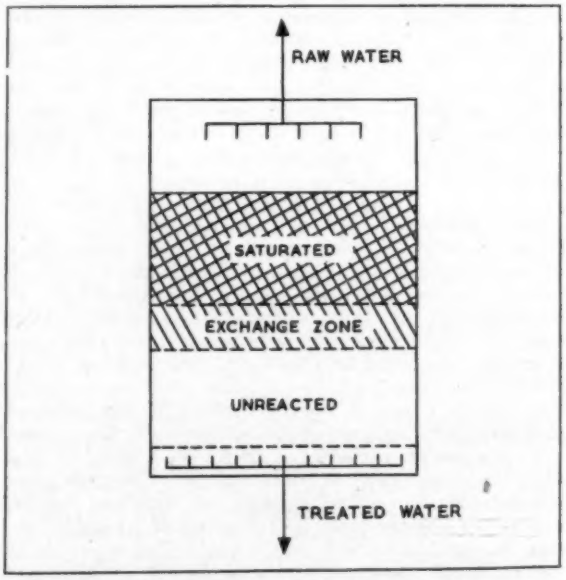


Fig. 5. Diagram of an Ion-Exchange Column.

waters and other solutions containing more than about 2000 ppm of dissolved electrolyte. For the continuous treatment of solutions containing lower concentrations of electrolyte, continuous column ion exchange is feasible although no commercial plants are yet available in this country.

To give an account of the numerous fields in which ion exchange has been applied would involve the danger of providing a mere catalogue and, therefore, no attempt has been made to do this. Suffice to say that it has been used in such diverse industries as antibiotics, sugar, glycerin, wine-making, metal finishing, electronics and hydrometallurgy and is finding many and varied uses in the field of atomic energy. While water treatment still constitutes by far the largest application, uranium recovery, to name only one other, accounts for a considerable number of exceptionally large installations. These applications outside the field of water treatment owe much to the modern ion-exchange resins with their greater versatility stemming from the various ion-exchange groups now available, greater capacity, and greater stability. The further developments in resins and techniques that can confidently be expected will extend still further the already wide field of application.

REFERENCES

[1] Adams, B. A., and Holmes, E. L. *J. Soc. Chem. Ind.*, 1935, **54**, 1T.
[2] Reents, A. C., and Kahler, F. H. *Ind. Eng. Chem.*, 1955, **47**, 75.
[3] Arden, T. V., in "Extraction and Refining of the Rarer Metals", *Inst. Mining & Metallurgy*, 1957, 119.
[4] Arden, T. V. *Nucl. Eng.*, 1956, 68.
[5] Burstall, F. H., Forrest, P. J., Kember, N. F., and Wells, R. A. *Ind. Eng. Chem.*, 1953, **45**, 1648.
Burstall, F. H., and Wells, R. A. "Ion Exchange and its Applications", *Soc. of Chem. Ind.*, 1955, 83.
Aveston, J., Everest, D. A., Kember, N. F., and Wells, R. A. *J. Appl. Chem.*, 1958, 77.
[6] Myers, P. B., Rouse, A. H., and Sardik Inc. U.S. Patent 2,323,483.
[7] The Permutit Co. Ltd., Pemberton, R. T., Walter, A. J., and Holmes, E. L. British Patent 553,233.
[8] Kressman, T. R. E. *Ind. Chem.*, 1954, **30**, 99.
[9] Volckman, O. B., *Brit. Chem. Eng.*, 1957, **2**, 146.
Moyers, W. H., and Volckman, O. B. *Trans. S.A. Inst. Civil Eng.*, 1957, **7**, 309.
Moyers, W. H. *Optima* (Anglo-American Corp. S.A.), 1957, 134.
[10] Nordell, E. U.S. Patents 1,608,611; 1,740,199.
[11] Hutcheon, J. M. "Ion Exchange and its Applications", *Soc. of Chem. Ind.*, 1955, 109.
[12] Peebles, F. N. *Chem. Eng. News*, 1956, 5200.
[13] Arehart, T. A., Bresee, J. C., Hancher, C. W., and Jury, S. H. *Chem. Eng. Prog.*, 1956, **52**, 353.
Higgins, I. R., and Roberts, J. T. *Chem. Eng. Prog. Sympos. Ser.*, 1954, **50**, No. 14, 87.
[14] McCormack, R. H., and Howard, J. F. *Chem. Eng. Prog.*, 1953, **49**, 404.
[15] Muendel, C. H., and Selke, W. A. *Ind. Eng. Chem.*, 1955, **47**, 374.

Rolling Extruder for Pretreatment of Pastes Prior to Drying

IN order to use conveyor driers effectively for paste-like materials discharged from filters or centrifuges, it is necessary to convert the pasty mass into a form which allows the drying air to circulate through it on the conveyor belt. A feeder is therefore required which allows the transformation of the sloppy cake into small agglomerates of uniform cross-section.

At first sight extrusion might seem a ready means to this end, but for some materials there are objections to the use of conventional extruders for this purpose. For example, in some cases the mechanical agitation with which the extruder is fitted may so soften the material that the extrusions lose their shape on leaving the die of the machine; in others, the agitation may cause the material to stiffen sufficiently to prevent extrusion.

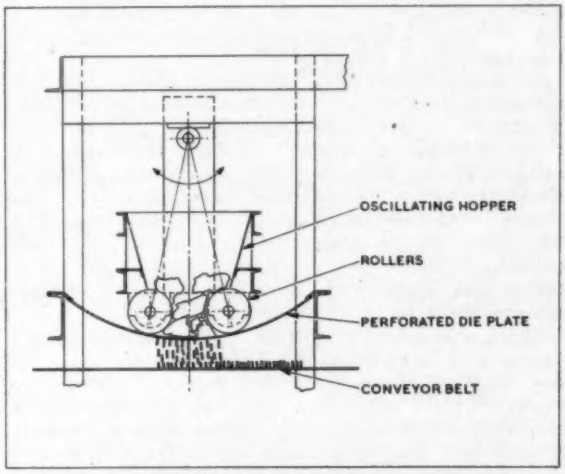
To overcome these difficulties a rolling extruder has been designed by Proctor & Schwartz, Philadelphia, U.S.A.,* its salient features being shown in Figs 1 and 2. It consists primarily of a rigid framework on which is mounted a perforated die plate (1) of accurate form and having the same width as the drier conveyor band. Over the die plate is mounted a hopper structure (2), whose lower part supports rubber-covered rollers (3). This structure is arranged to reciprocate slowly over the die plate with which the rollers are in light rolling contact. Material in the hopper, provided it is suitably plastic, will be directed between the die plate and the rollers as they move back and forth, thereby forcing extrusions of equal cross-section and substantially equal length through the die plate in a random manner on the conveyor band below.

The depth of bed of the material discharged to the conveyor belt can be varied by controlling the speed of the conveyor band or by altering the reciprocating speed of the hopper. Since the working width of the extruder is the same as that of the conveyor, the extrusions are spread evenly over the latter. The interstices between the extruded cylinders provide a path for the drying air and the considerable surface exposed to the drying medium ensures rapid and uniform drying.

This type of extruder developed by Proctor & Schwartz Inc. has proved highly successful for the treatment of precipitates with thixotropic and dilatent properties which hitherto have been considered unsuitable for extrusion.

Current applications, where the extruder is a component of conveyor drier units, include extrusion of filter cakes composed of titanium dioxide, iron oxide, lithopone, metallic stearates and other.

* The equipment is available in this country from John Dalglish & Sons Ltd., Thornliebank, Glasgow.



A diagram of the rolling extruder and a view showing the perforated plate, hopper and rollers.

66.064: 551.464: 551.481

LARGE-SCALE DEMINERALISATION OF SEA AND BRACKISH WATER PART II — MEMBRANE PROCESSES*

The authors discuss three electrodialysis processes employing membranes and give some details of plant costs

by A. M. ESHAYA, D.Eng., and B. F. DODGE, D.Sc.

IN the first article of this series some of the general problems of large-scale demineralisation of sea water were examined and the more important distillation schemes used for this purpose were discussed.[1] In these processes the barrier used for achieving the desired separation is the phase interface, and considerable heat energy is required to move the water molecules across this barrier. Another characteristic of the vaporisation processes is that they remove large quantities of water away from the relatively small quantities of salt.

If, instead of the phase interface, a barrier such as a membrane were used to obtain the separation, no phase change would be involved, and the transport of water could be achieved by the application of electrical or mechanical energy. Furthermore, such processes may be made to operate on the small quantities of salts and remove those from the large body of water rather than the reverse, with resulting economic advantages. One such process, known as electrodialysis, is based on the use of cation- and anion-permeable membranes in an arrangement shown in Fig. 1 (a), (b), and (c).

The concentration of Na^+Cl^- is uniform throughout the cell as long as no current flows in it [Fig. 1 (a)]. As soon as a d.c. voltage is applied between the two electrodes E^+ and E^- [Fig. 1 (b)] the cations begin to migrate toward the negative electrode. Their movement, however, is checked at the first anion-permeable membrane which they encounter. The anions move in the opposite direction until they meet a cation-permeable membrane. The result is a depletion of Na^+Cl^- ions from the even-numbered compartments and their concentration in the odd-numbered ones.

Importance of Membrane

Clearly, the most important part of any electrodialysis system is the membrane. The action of selectively permeable membranes is based on the GIBBS-DONNAN membrane equilibrium. A high concentration of ionic groups present in the membrane prevents the diffusion of ions of the same charge through the membrane. A discussion of the GIBBS-DONNAN membrane equilibrium and of membrane transport processes is beyond the scope of this paper. For an analysis of these processes the reader is referred to References 2, 3, 4, 5 and 6. It should be noted that while the GIBBS-DONNAN equilibrium phenomena are amenable to treatment by the methods of classical thermodynamics, the more complex processes occurring in a flow system at steady state are being approached with success by means of non-equilibrium thermodynamics, in which a description of the system is given in terms of the thermodynamic equations of motion of the form

$$J_i = \sum L_{ik} X_k$$

where J_i is a generalised flux, L_{ik} is a generalised conductance and X_k is a generalised force.[2, 4, 7, 8] The specific combinations of forces and fluxes are selected in such a way as would be consistent with the ONSAGER reciprocal relations of the type $L_{ik} = L_{ki}$.

Desirable properties of membranes for application to large-scale demineralisation of saline water include high electrical conductivity, low permeability to the passage of water, high selectivity to either anions or cations, good mechanical strength, good chemical stability to any trace impurities in the water such as H_2S or Fe, and low cost. Some of these requirements are incompatible with each other and a compromise is necessary in arriving at a membrane satisfactory from the overall point of view. The picture is further complicated by the fact that the desirable characteristics of a membrane are influenced to a large degree by the concentration of the solution being demineralised.[11] The above explains the great variety of membranes which are being used or are under investigation for use in large-scale demineralisation units.

The first ion-selective membranes were the naturally-occurring ones of plant and animal origin. The collodion membranes prepared by MICHAELIS (see review paper by SOLLNER[26]) were probably the first to be synthethised. SOLLNER and co-workers were successful in preparing films which were not only highly ion-selective but also of high ionic-permeability.[9] A great variety of membranes of different characteristic properties has been developed since then. These membranes fall into two general categories—homogeneous and heterogeneous. The first are essentially cross-linked resins and are characterised by high ion concentrations which account for their very high selectivity. Their mechanical properties are, however, generally unsatisfactory, unless the degree of cross-linking is decreased, and this results in a loss of selectivity and higher ohmic resistance. The heterogeneous membranes are prepared by

* Part I was published in the April 1959 issue, p. 194.

C = CATION – PERMEABLE MEMBRANE
A = ANION – PERMEABLE MEMBRANE
E = ELECTRODE

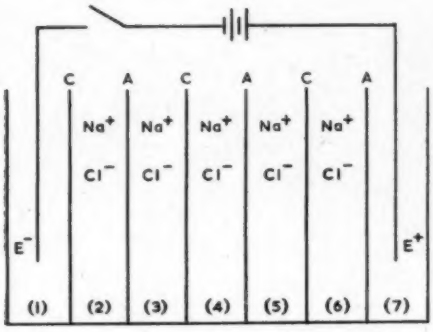


FIG. 1a

Uniform concentration of ions.

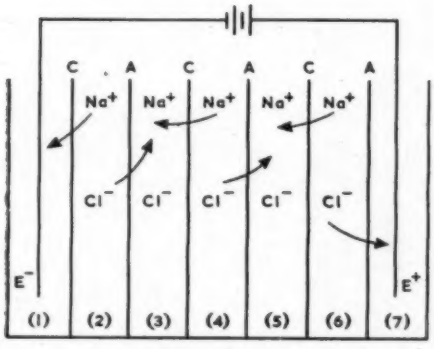


FIG. 1b

Ions about to migrate on application of d.c.

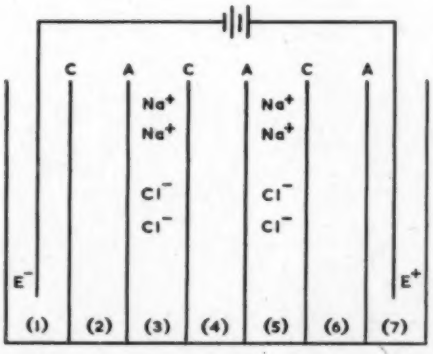


FIG. 1c

The concentration of Na^+ and Cl^- ions takes place. The principle of the osmionic process.

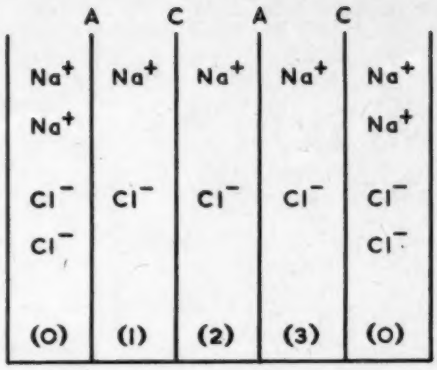


FIG. 2a

Initially, compartments 1, 2 and 3 have a brine concentration C_1. Compartment 0 has a concentration $C_2 > C_1$.

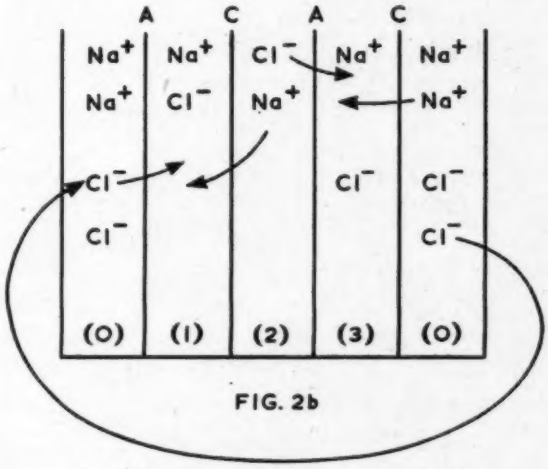


FIG. 2b

The concentration gradient causes Cl^- and Na^+ ions to pass into compartments 1 and 3 respectively.

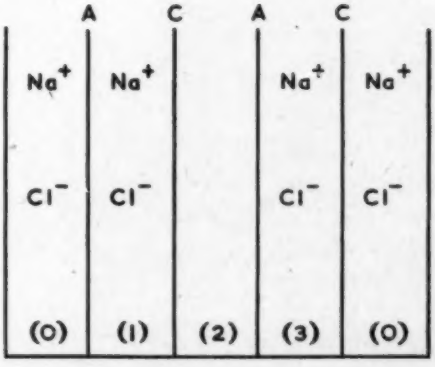


FIG. 2c

Cl^- ions from compartment 2 diffuse into compartment 3, and Na^+ ions pass from 2 into 1, causing a decrease of NaCl in 2.

incorporating ion-exchange resin particles in an inert plastic matrix. Such membranes can be prepared by continuous and relatively inexpensive processes; however, they also have certain disadvantages: their ohmic resistance is high and relatively thick films are needed to give the necessary mechanical strength. Dimensional instability due to swelling of the resin particles may lead to rupture. A relatively new type known as interpolymer membranes has been developed by GREGOR[11, 12] by casting a film from a homogeneous solution of two polymers, one a polyelectrolyte or an ionogenic polymer, the other a water-insoluble film-forming plastic.

Some examples of the ionic groups incorporated in membranes include quaternary ammonium anion-permeable membranes,[2] sulphonated cross-linked polystyrene resins,[13] polythene films treated with chlorosulphonic acid,[14] films containing positively charged sulphonium groups,[15] pyridinium membranes prepared by treating parchmentised paper with a suitable pyridinium compound,[17] etc. The concentration of functional ionic groups in the membranes depends largely on the type of membrane and the mode of preparation and it may vary anywhere from 1 to 7 molal.

Calculating Energy Requirements

The problem of calculating the energy requirements for an electrodialysis process is much more complicated than the similar problem for distillation processes. In addition to the parameters pertinent to the membrane itself, one has to consider the spacing between the membranes, the linear velocity of the fluid past the membranes, the concentrations of the salt in the fluid on the two sides of the membrane, and the current density. The total energy requirement involves two terms—the energy required to move the ions from one fluid stream to the other and the mechanical energy needed to pump the brine and dialysate past the membranes. The former may be calculated from the following equation which can be derived from Faraday's and Ohm's Laws:[10]

$$W_e = K\frac{IR_sC_of F}{\varepsilon n} \qquad \ldots.(1)$$

where W_e = energy needed to demineralise a given volume of brine;
K = constant depending on units used in equation;
I = direct current flowing through membrane stack;
C_o = concentration of brine entering diluting cell;
f = fraction of electrolyte transferred across membrane;
F = Faraday's constant;
ε = current efficiency of a cell;
n = number of cells in stack; and
R_s = electrical resistance of stack.

Equation (1) shows that the energy required to demineralise a given volume of brine is proportional to the initial brine concentration C_o, and inversely proportional to the final dialysate concentration through the term f, since a large f corresponds to a low dialysate concentration.

For an ideal membrane,* i.e., one having perfect conductivity and ion selectivity, MURPHY[4] has obtained the following relationship:

$$W_e = KC_o\frac{C_c - C_d}{C_c + C_d}\ln\frac{C_d}{C_c} \qquad \ldots.(2)$$

where K = constant depending on temperature, brine velocity, and linear dimensions of membrane cells;

* The assumption of an ideal membrane should not be confused with the assumption of an ideal, i.e., reversible process.

TABLE 1—Energy Requirements for Electrodialysis by Ideal Membranes

Brine velocity, cm/sec.	Energy Requirement, kWh per 1000 gal.					
	$C_c:C_d = 1000$			$C_c:C_d = 10$		
	W_e	W_m	$W_e + W_m$	W_e	W_m	$W_e + W_m$
10^{-3}	21.6	≈0	21.6	5.90	≈0	5.90
1	21.6	≈0	21.6	—	—	—
10	21.6	0.16	21.7	5,92	0.13	6.05
50	22.2	2.1	24.1	6.21	1.44	7.69
100	23.7	5.6	29.3	6.85	3.37	10.22
300	34.4	20.4	54.8	—	—	—
1000	82.1	70.5	152.6	—	—	—

C_c = concentration of waste stream; and
C_d = concentration of dialysate.

Equation (2), like Equation (1), shows the dependence of W_e on the concentrations of the stream which enter (C_o) and leave (C_c, C_d) the cell.

The mechanical energy term, W_m, is calculated simply from hydrodynamic theory assuming streamline flow between the membranes:

$$W_m = 12\,\eta\,u\frac{y}{d^2} \qquad \ldots.(3)$$

where η = viscosity of brine;
u = linear velocity of brine past membrane;
y = dimension of membrane in the direction of flow; and
d = distance between two membranes.

TABLE 2—Energy Requirements for Electrodialysis of Saline Waters

C_o, initial concentration, ppm salts	C_d, dialysate concentration, ppm salts	Energy required, kWh per 1000 gal.	Reference
1800	500	8	18
8800	1000	9*	16
8000	500	35	18
22000	500	110	18
32000	500	135	18

* Excluding pumping and losses in rectifying of current.

Using Equations (2) and (3), MURPHY[4] and MURPHY and TABER[3] have calculated W_e and W_m for linear velocities of $10^{-3} < u < 10^3$ cm/sec., $C_o = 6{\cdot}4 \times 10^{-4}$ equivalents per cm³, and $Cc:Cd$ of 10 and 1000. The results of these calculations are shown in Table 1.

The effect of brine velocity on W_e is through the constant, K, of Equation (2) which varies with u in a complex way. The effect of u on W_m is obvious from Equation (3); it should be remembered, however, that for a constant volumetric flow rate an increase in u brings about an increase in the y/d^2 term, so that the effect of u on W_m is more than linear as shown by the figures in Table 1. In general, W_m is an appreciable energy term in electrodialysis plants.[19] As might be expected the energy requirements measured in existing installations are considerably higher than the ideal membrane values. Table 2 shows some figures obtained in actual operation of several electrodialysis plants.

It is difficult to compare directly the figures of Tables 1 and 2 because of the differences in the concentrations involved. Unfortunately, information is not available to permit the reduction of the actual plant data shown in

Table 2 to the same basis as that used in the calculations leading to the results summarised in Table 1. Qualitatively, however, one may compare the 7·69 kWh of Table 1 ($C_o:C_d = 10$; $u = 50$ cm/sec) with the 35 kWh of the third line of Table 2. Similarly, one may consider 24·1 kWh ($C_o:C_d = 1000$; $u = 50$ cm/sec) in relationship to 135 kWh required by a plant which produces a dialysate of 500 ppm salts from sea water feed.

For desalting brackish waters of up to 8000 ppm salinity the energy requirements of the electrodialysis process are lower than those of the vapour-compression or multiple-effect distillation plants.[1] At concentrations approaching those of sea water, the energy requirements for electrodialysis become much higher than those for distillation processes. This characteristic of the electrodialysis process restricts its usefulness to the demineralisation of brackish waters.

Considering again Equation (1), it is seen that the energy requirement, W_e, for the demineralisation of a given volume of brine, is directly proportional to the current or current density. W_e can be reduced by reducing I, but only at the cost of reducing plant capacity which is directly proportional to I. One is thus faced with the familiar situation of having to select an optimum combination between energy requirements and fixed costs. In the case of dialysis, however, a further complication arises from the fact that the optimum (from the energy point of view) current density is a function of the concentrations. Thus for a given electrodialyser operating on a feed of 33,000 ppm NaCl and producing dialysate of 500 ppm NaCl, the estimated optimum current density is 40 mA/sq. cm equivalent to a capacity of 670 gph with an energy requirement of 150 kWh per 1000 gal. For the same unit operating on a feed of 8250 ppm NaCl, and a dialysate of 500 ppm NaCl, the estimated optimum current density is only 20 mA/sq. cm, equivalent to a capacity of 1330 gph with an energy requirement of 30 kWh.[20] Thus energy requirement, plant capacity, feed and dialysate concentrations are seen to be interrelated. By comparison, in a distillation plant, feed concentration and product concentration do not enter the optimisation calculations.

Plant Costs

Because of the relative newness of electrodialysis plants, cost information is rather scant. On the basis of extensive field tests SIEVECA[19] has estimated actual costs of dialysate produced in a 25,000-gpd plant to be $1.30 and $1.10 per 1000 gal. for feeds of 4000 and 2000 ppm solids respectively, with a final dialysate concentration of 250 ppm. Increase of the plant size to 1,500,000 gpd may be expected to lower these figures to $0.80 and $0.60. Of the total cost, from 30 to 45% is attributable to fixed charges, from 22 to 35% is energy cost, and the remaining is the cost of membrane replacement. These figures are higher than the target cost considered as a realistic goal by the Office of European Economic Co-operation in 1953,[25] but the gap may be expected to be narrowed with technological improvements.

In addition to the very important question of cost reduction, progress has been made in overcoming some serious operational difficulties due to the formation of calcium carbonate scale on the concentrating face of the anion-transfer membranes. This scale leads to increased electrical resistance and gradual physical deterioration of the membrane. Eventually the accumulated deposits lead to blocking of the passages and rupture of the membranes. Continuous addition of acid to the concentrating cells eliminates this scale at a cost of about 2 to 3 cents per 1000 gal. Calcium sulphate scaling is controlled by avoiding supersaturation in the concentrating stream through the use of a high blowdown-to-product ratio. When formed in small quantities, this scale has been found to be in a loose form easily removed by flushing. Reversal of polarity for periods of 5 to 6 hr has been found effective in regenerating membranes on which a scale had been formed. Scaling on the cathode can be reduced to acceptable levels by special rinses, such as sodium sulphate, by p_H adjustment, or by the introduction of sequestering agents in the cathode compartments.[16] Pretreatment of the feed stream to remove solids is recommended for satisfactory operation. For feed waters containing 1·0 ppm of iron or more, removal of the iron by oxidation and filtration is necessary in order to prevent the formation of a deposit of brown slime on the membranes. High concentrations (60 ppm) of H_2S have also been found to be deleterious to membrane stability.[18]

Although a relatively new development, the number of installations for the large-scale demineralisation of saline waters by electrodialysis has been increasing rapidly. At present there are approximately 20 plants producing demineralised water by this process. Capacities of these plants vary from 2000 gpd of small experimental units to 2,400,000 gpd at the plant of the Free State Geduld Mine. Because of the reasons already touched upon in the previous sections, only five of these plants (with combined capacity of about 12,000 gpd) operate on sea water feed; the rest are used in the demineralisation of brackish waters. Batch treatment is used in the smaller units, with continuous processing becoming more economical at a capacity of about 25,000 gpd.

The Osmionic Process

A process which is closely related to electrodialysis is the osmionic process suggested first by MURPHY.[21] If a saline water of concentration C_1 has a vapour pressure of p_1, the minimum energy requirement to transport the water from this solution to pure water of vapour pressure, p_0, is given by the free energy increase:

$$\Delta F = RT \ln \frac{p_0}{p_1} \quad \ldots . (4)$$

Now if saline water of concentration C_2 and vapour pressure p_2 is available (where $C_2 > C_1$) the transfer of water from C_2 to C_1 is accompanied by the free energy decrease

$$-\Delta F = RT \ln \frac{p_2}{p_1} \quad \ldots . (5)$$

and this is available to provide work. By suitable choice of C_2 the work yield can be made to balance the work requirement and at the limit, i.e., for reversible processes, no net input of external work is required. The manner in which the above principle may be exploited is made clearer by referring again to Fig. 1 (c). We note that the concentration differences in adjacent compartments were brought about by the passage of direct current from one electrode to the other. If one started with a cell in which the adjacent compartments contained brines of different concentration and then completed the electrical circuit externally the concentration in the adjacent compartments would tend to equalise and a current would flow in the circuit as a result of the electrical potential which would be developed by what is essentially a concentration cell. This current may conceivably be used to drive an electrodialysis unit for the demineralisation of saline water. The external circuitry can be avoided and the concentration difference of the first cell used directly to demineralise water in an arrangement such as shown in Fig. 2. At the beginning, compartments 1, 2 and 3 are filled with a brine concentration C_1 and compartment 0, which surrounds compartments 1, 2 and 3, is filled with concentrated brine at concentration $C_2 > C_1$. Because of the concentration gradient Cl^- and Na^+ ions from compartment 0 diffuse into compartments 1 and 3 respectively [Fig. 2 (b)]. Maintenance of electrical neutrality

in these compartments requires that simultaneously with this process another one must occur—that of diffusion of Cl^- from 2 to 3 and Na^+ from 2 to 1. The net result is the decrease in concentration of NaCl in compartment 2 [Fig. 2 (c)]. The process is seen to require a source of brine of higher salts concentration than the one which is to be demineralised. This could conceivably be obtained by solar evaporation of sea water or from brine wells.

Since the osmionic process is in its early stage of laboratory experiments, it is difficult to evaluate its future potential. For a more detailed discussion of the theory and experimental results the reader is referred to the excellent summaries presented in References 21 and 22.

Reverse Osmionic Process

A third process which involves the use of membranes is the ultra-filtration or reverse osmosis process. When a salt solution is in contact with a membrane which is permeable only to water and impermeable to the various ions, it is possible, by applying on the salt water pressure greater than the osmotic pressure, to force demineralised water through the membrane. The process differs from electrodialysis in two important aspects: the nature of the membrane and the form of the energy used in the process. In the reverse osmosis process the membranes do not have to be ion-selective, i.e., the discrimination needed is that between water molecules and salt ions, and not between anions and cations. The energy is supplied in the form of pressure, i.e., mechanical and not electrical energy. The osmotic pressure of sea water is about 23 atm. and, assuming that a part of the mechanical energy of the compressed water is recoverable, REID[23] has calculated an energy requirement of 15 kWh per 1000 gal. for the purification of sea water. Since 23 atm. is the equilibrium pressure, i.e., the pressure necessary to equalise the activities of the water on the two sides of the membrane, the rate of transport at this pressure will be nil. Furthermore, the pressure of 23 atm. is for 0% recovery of pure water from normal sea water. As the per cent recovery is increased the water has to be removed from a solution of higher salt concentrations and consequently the pressure is higher. For a 50% recovery, the osmotic or equilibrium pressure is 46 atm. and for 80% recovery it is 100 atm. In any practical installation the pressures involved will be considerably higher than the osmotic pressure. This leads to one of the difficult problems in the application of reverse osmosis, namely, the development of membranes which can operate at the necessary high pressures for prolonged periods of time. Experiments with cellulose acetate at 40 atm. pressure resulted in membrane failures in less than one hour.[23] There were indications that at high pressure these membranes became slightly permeable to NaCl, reducing the salt content of the brine by about 95% rather than eliminating it completely. Cellophane films are even more permeable to salts rejecting only 40% at 330 atm.[23]

A serious difficulty with the reverse osmosis process is the low permeability to water of salt-restraining membranes. Basically the process is one of filtration requiring very small membrane pores, which inevitably means a low flow rate for a given pressure difference. Flow rates measured with cellulose acetate membranes are approximately 3×10^{-3} ml per hr per cm^2 per atm. pressure difference.[26] Assuming that it will be possible to develop films of cellulose acetate, or any other material, which will operate at this rate for prolonged periods of time, the membrane area required for a 100-gph plant, operating with a 40 atm. pressure difference across the membrane, will be 34,200 ft^2. A distillation plant of the same capacity will require not more than 1500 ft^2 of heat exchanger surface. Development of membranes which make possible higher rates without decreasing the effectiveness of the salt rejection appears to be one of the major problems which has to be solved if the process is to become of industrial significance. The very preliminary nature of the work which has been done thus far on the reverse-osmosis process does not warrant any further speculation concerning its potential applicability to large-scale water demineralisation. By virtue of its simplicity, however, this process is an appealing one. It should be noted that the reverse osmosis process differs from electrodialysis and the osmionic process in that it removes water (and not salt) from the brine and in this respect resembles the vaporisation processes.

The preceding discussion has shown that, of the three processes employing membranes for the demineralisation of sea water, one at least—electrodialysis—has been developed sufficiently to justify its use in large-scale installations. This process is particularly well suited for the demineralisation of brackish waters containing less than 10,000 ppm of salts. In this application it appears to have an economic advantage over existing distillation processes. As far as demineralisation of sea water is concerned, the rapid increase in the energy requirements of the electrodialysis process with salt concentration makes it unlikely that it would be able to compete with distillation in the forseeable future.

In the concluding article of this series, attention is focused upon a distillation process for the economic large-scale demineralisation of sea water. This process is based upon a vapour-compression cycle and condensation is made to occur dropwise.

REFERENCES

[1] Eshaya, A. M., and Dodge, B. F. *British Chemical Engineering*, 1959, **4**, 4, 194.
[2] Duncan, B. C. "The Principles of Electrodialysis", Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D.C., 1957.
[3] Murphy, G. W., and Taber, R. C. "Non-equilibrium Thermodynamics of Transference Cells, Cells Without Transference and Membrane Demineralisation Processes", ibid., p. 196.
[4] Murphy, G. W. "The Minimum Energy Requirements for Sea Water Conversion Processes"; Office of Saline Water, Research and Development Program Report, No. 9, April, 1956.
[5] Staverman, A. J. *Trans Faraday Soc.*, 1952, **48**, 176.
[6] Staverman, A. J. *Chem. Weekblad*, 1951, **47**, 1.
[7] Denbigh, K. G. "The Thermodynamics of the Steady State". Methuen & Co. Ltd., London, 1951.
[8] DeGroot, S. R. "Thermodynamics of Irreversible Processes". North-Holland Publishing Co., Amsterdam, 1958.
[9] Sollner, K. *J. Electrochem. Soc.*, 1950, **97**, 139 C.
[10] Applied Science Laboratories Inc., Final Report to Office of Saline Water, U.S. Dept. of the Interior, October 1, 1957.
[11] Gregor, H. P. "Interpolymer Ion-selective Membranes", Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D.C., 1957, p. 240.
[12] Gregor, H. P., Jacobson, H., Shair, R. C., and Wetston, D. M. *J. Phys. Chem.*, 1957, **61**, 141.
[13] Hookway, H. T. "The Development of Membranes for Electrodialytic Processes", Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D.C., 1957, p. 233.
[14] Belgian Patent 537,438.
[15] U.S. Patent 2768990.
[16] Volkman, O. B., and Moyers, W. H. "Ion-selective Membrane Research and Electrodialysis Engineering Development in the Union of South Africa", Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D.C., 1957, p. 283.
[17] South African Patent 17366.
[18] Juda, W., Kirkham, T. A., Mason, E. A. "Field Operation of Electric Membrane Equipment for Water Desalting", Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D.C., 1957, p. 265.
[19] Sieveka, E. H. "Summary of Developments in Electrodialysis", ibid., p. 255.
[20] Wegelin, E. "Multi-compartment Electrodialysis and its Technical Development", ibid., p. 259.
[21] Murphy, G. W. The Osmionic Process, Office of Saline Water Research and Development Progress Report No. 14, 1957.
[22] Lacey, R. E. "Development of the Osmionic Process and Factors Influencing the Choice of Membranes"; Proceedings of the Symposium on Saline Water Conversion, Office of Saline Water, U.S. Dept. of the Interior; Publication 568 of National Academy of Sciences—National Research Council, Washington, D. C., 1957, p. 224.
[23] Reid, C. E. "Osmotic Membranes for Demineralization of Saline Water", ibid., p. 238.
[24] Sollner, K. Review Article, *J. Phys. Chem.*, 1945, **49**, 47.
[25] Office of European Economic Co-operation Press Release D (53) 10: August, 1953.
[26] Breton, E. J. "Water and Ion Flow Through Imperfect Osmotic Membranes", Research and Development Progress Report No. 16, Office of Saline Water, U.S. Dept. of the Interior, April, 1957.

66.012-987

HIGH PRESSURE CHEMISTRY — PART 2*

The effects of very high pressure upon rates, yields and the products of chemical reactions

by W. STRAUSS, M.E., M.Sc.

AN increase in temperature almost invariably increases the velocity of a chemical reaction to a marked extent. For homogeneous processes the specific rate is approximately doubled or trebled for each 10°C rise in temperature. The effects of pressure are more complex, but from the large number of rate measurements carried out in the last 30 years a fairly definite pattern has emerged, and it is now possible to predict qualitatively the effect of pressure on some types of solution reactions.

The equilibrium constant K in a chemical reaction is related to the molar volume change, $\triangle V$, by the relation

$$RT\ (\delta \ln K/\delta P)_T = -\triangle V$$

where P is the pressure and T the absolute temperature. VAN'T HOFF, in 1901, suggested an analogous relation for a chemical reaction in which the rate constant, k, is related to the pressure by the equation

$$RT\ (\delta \ln k/\delta P)_T = -\triangle V^*$$

where $\triangle V^*$ is the volume change when the reactants are converted into the activated state. In its more modern form, the concept of the activated state was put forward by EVANS and POLANYI in 1935. These authors pointed out that the volume change is composed of two components:

(i) the actual volume difference between the molecules in the activated state and the reactant molecules, $\triangle_1 V$; and

(ii) the volume change brought about by the differing solvent interaction with molecules or ions of the reactants and with the fully (or partially) ionised transition state; $\triangle_2 V$.

Recent work has shown that when there is a change in the number of ions in a chemical reaction, or when there is an ionised transition state, $\triangle_2 V$ is the predominant effect.

Reactions where there is an increase in the number of ions are accompanied by large negative entropies of activation (25-35 cal./deg. mol.) which almost certainly represent the entropy lost by the solvent molecules frozen around the transition-state molecules, and causing a diminution in the total volume of the solution.

Generalisations in agreement with experimental data for the effect of pressure on ionic liquid-phase reactions can be summarised as follows:

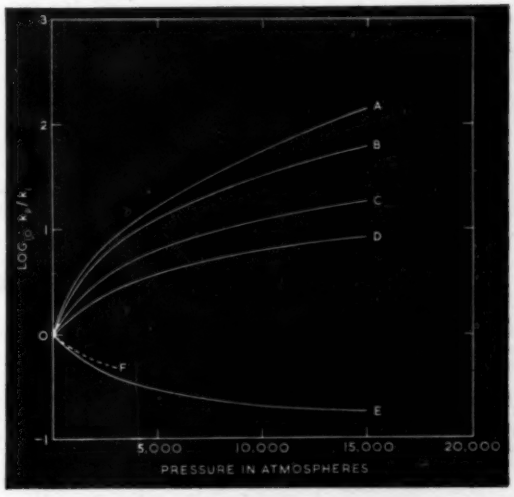


Fig. 1. The effect of pressure on the various types of solution reactions. The logarithm of the ratio of the rate constants is plotted against a pressure abscissa.†

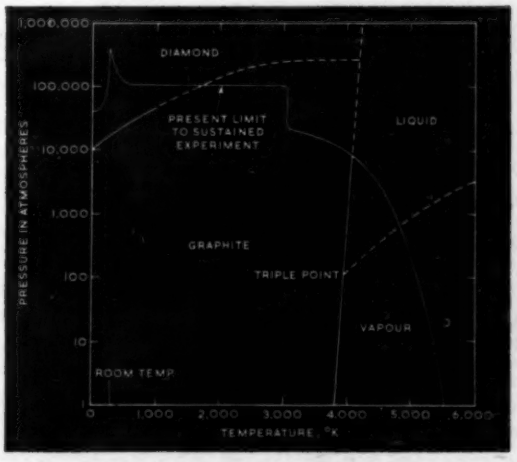


Fig. 2. The carbon phase diagram.[5]

---

* Part 1 was published in the July issue, p. 386.

†Reaction I: Solvolysis of Ethyl Chloride with Methanol. Reaction II: Solvolysis of Ethyl Bromide with Methanol. Reaction III: Solvolysis of Ethyl Iodide with Methanol.[4] These are reactions where ions are formed during the reaction.

Reaction IV: Solvolysis of Ethyl Bromide with Sodium Methoxide. No new ions are formed during this reaction.

Reaction V: Formation of Urea from Ammonium Cyanate.[7] There is a decrease in the number of ions for the reaction.

Reaction VI: Decomposition of Benzoyl Peroxide into Free Radicles.[8] The formation of free radicles.

(i) when ions are formed in the rate-determining step of a chemical reaction (even if this is only an ionised transition state with neutral end products) the speed of the reaction will be considerably increased by pressure;

(ii) when there is no change in the number of ions involved, there will be a much smaller pressure effect; and

(iii) when there is a decrease in the number of ions in the rate-determining step, the reaction will be slowed down by increases in pressure.

In free radical reactions (where no ions are involved) the $\triangle_1 V$ term is the predominant one. If the rate-determining step is the formation of free radicals from a molecule, involving the fission of a homolytic bond, there is a decrease in rate with increasing pressure.

Reactions in the first category have been more systematically investigated than in the others, as the results have been more spectacular, and further conclusions can therefore be drawn from the experimental work. In a series of reactions of the same type in the same solvent—the solvolyses of ethyl halides in methanol—the effect of pressure on the rate is less marked as one proceeds from Cl through Br to I. The smaller ion has a greater solvation energy, which, in turn, is more affected by the compression of the solvent (Table 1).

In a reaction with the same molecules but in a different solvent, the rate is affected by the pressure dependence of the dielectric constant of the solvent. The dielectric constant of acetone is increased by 17.5% over 3000 atm., while that of methanol by only 15.7% over the same pressure range. The reaction of NN dimethyl-*o*-toluidine with methyl iodide is increased by a factor of 10.9 in acetone, but only by a factor of 6.9 in methanol.[1] This change can be predicted by using a simple bulk solvation model.[2] The solvolysis of allyl bromide in methanol, which is also in this class, has been measured to 45,000 atm. at 23°C, and an increase in rate of almost 2000 times was found.

Polymerisation

Pressure may favour the formation of polymers such as polyethylene, which may be of great commercial importance. In certain cases, when almost negligible yields are obtained at atmospheric pressure, high yields can result at high pressures or a polymer of greater commercial value may be obtained. This has led to much exploratory work on high-pressure polymer formation. Early measurements were concentrated on attempts to produce a synthetic elastomer, usually by the pressure polymerisation of isoprene, the fundamental rubber molecule. The conclusion reached was that monomers with conjugated double bonds polymerised, while those with adjoining double bonds did not. It was also found necessary to provide a catalyst as a chain reaction initiator in the form of dissolved oxygen or benzoyl peroxide.

In only one case has a complex polymerisation been fully investigated at high pressures. This is the benzoyl peroxide catalysed polymerisation of styrene. Its rate increases about tenfold, exponentially, over a range of 5000 atm. The average molecular weight of the polymer increases about tenfold, exponentially, over a range of 5000 atm. The average molecular weight of the polymer increases to about 3000 atm., above which it remains constant. The mechanism of polymerisation can be divided into three stages:

(i) initiation of the polymerisation due to decomposition of the catalyst, benzoyl peroxide, into its free radical components;

(ii) propagation of the chain reaction; and

(iii) termination of the chain.

TABLE 1—The Effect of Pressure on the Solvolyses of Ethyl Halides in Methanol at 65°C*

Reaction	k_{2000}/k_1	k_{15000}/k_1
Solvolysis of C_2H_5Cl	7.9	136
Solvolysis of C_2H_5Br	5.4	60
Solvolysis of C_2H_5I	4.7	19

* From HAMANN and TEPLITZKY.[3]

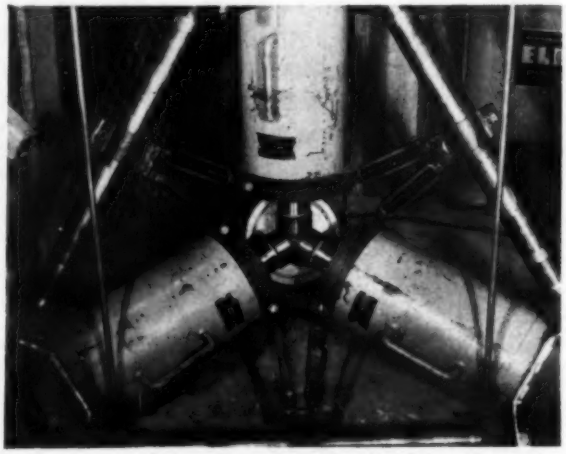


Fig. 3. A view of the tetrahedral anvil apparatus used at the Brigham Young University, Utah, for reactions at very high pressures.

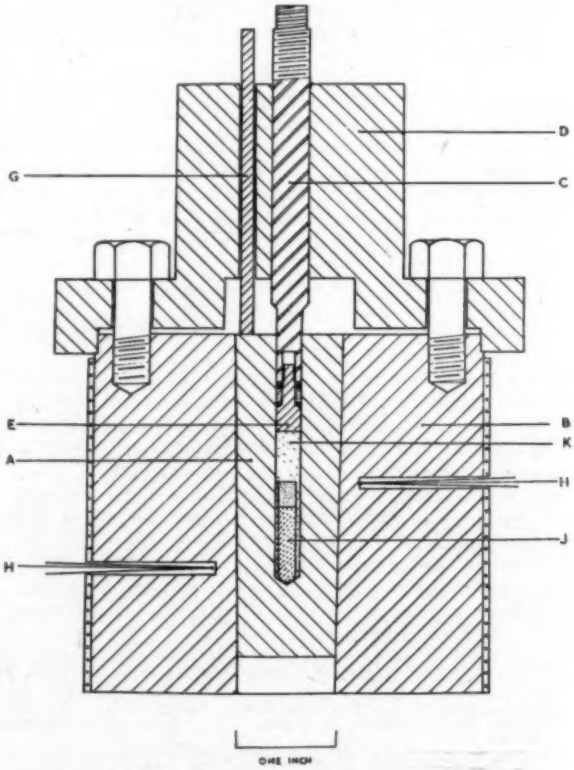


Fig. 4. Sectional view of high-pressure vessel used by Hamann for pressures up to 20,000 atmospheres.

From the discussion of the effect of pressure on free radical reactions, it may be seen that stage (i) is slowed down by pressure. Stage (iii) is found to be relatively unaffected by pressures, particularly above 1000 atm., prior to which it was decreased. Stage (ii), the chain propagation, is greatly increased by increases in pressure, and in this case is the predominant effect. The high pressures align the styrene molecules, which assists in this process.

The general effect of pressure on polymerisation has been summed up by HAMANN[3] as follows:

(1) The molecular weight of a polymer increases with pressure. While some monomers will only dimerise at ordinary pressures, they will give considerable yields of a high molecular weight polymer at pressures of a few thousand atmospheres.

(2) Although in general the structure of a polymer is unchanged by high pressures, it is sometimes possible to build in new groups at these pressures. This has been possible in the free radical copolymerisation of ethylene with carbon monoxide in methanol solutions. Chemically-bound methanol is incorporated in the molecule when the process is carried out at high pressures—8% at 3000 atm. and 27% at 8000 atm.

(3) Pressure can bring about polymerisations normally hindered by steric reasons.

Polyethylene. The most important high-pressure polymerisation carried out commercially at present is the polymerisation of ethylene. This was first discovered by I.C.I. in 1933, when it was passed over, as the equipment in which it was produced exploded and no further work could be done. The process was rediscovered late in 1935, and a few months later the first patents were taken out. The discovery was actually a "by-product" of the extensive observations on the influence of pressure on chemical reactions which were carried out at the Research Department of I.C.I. (Alkali) Ltd., Northwich, which were the most comprehensive at the time.[4] "Polythene" or "alkathene" has been produced commercially since about 1939, and the first orders were for using it as an insulator for electric cables, although since then it has become the most universal packaging medium, with an annual production of millions of tons. The process consists essentially of passing ethylene together with a small amount of oxygen to act as catalyst through a reactor at 200°C and at about 1500 atm. The oxygen helps to form free radicals which initiate the reaction.

$$R^* + CH_2{:}CH_2 \longrightarrow R.CH_2.CH^*_2$$

which then reacts with further ethylene molecules

$$R.CH_2.CH^*_2 + n\ CH_2{:}CH_2 \longrightarrow R(CH_2)_{2n+1}.CH^*_2$$

and may be terminated either by the disproportionation reaction

$$R.(CH_2)_n.CH^*_2 + CH^*_2(CH_2)_m.R \longrightarrow R.(CH_2)_{n-1}CH{:}CH_2 + R.(CH_2)_m.CH_3$$

or by the self-neutralisation

$$R.(CH_2)_n.CH^*_2 + CH^*_2(CH_2)_m.R \longrightarrow R.(CH_2)_{n-m+2}.R$$

As it is important to produce long chain molecules, the second of these four reactions, the chain propagation, must be accelerated. This is done by increasing the ethylene concentration by increasing the pressure.

In the case of polyethylene, it has been possible to find a catalyst which will assist the polymerisation to take place at atmospheric pressure, and dispense with the need for employing high pressures. This process, the "Ziegler" process, produces a different type of polyethylene, which is much harder than the high-pressure product.

Diamonds

These articles have been wholly concerned with chemical changes at high pressure, but two physical changes with increasing commercial possibilities must be added: the "growing" of quartz crystals used in radar and television transmitters, which is carried out by the General Electric Co., and the making of diamonds for industry.

Diamond is 1.6 times as dense as graphite, and various attempts to make diamonds by compressing graphite or other carbon compounds have been recorded. The best known of these are by J. B. HANNAY (1880) and HENRY MOISSAN (1894). MOISSAN dissolved sugar charcoal in molten iron and quenched the solution in cold water, which was to crystallise the carbon under the great pressure generated as the iron cooled from the outside. The metal was dissolved from the solidified melt, and traces of transparent material, with optical properties similar to diamond, remained. HANNAY sealed mixtures of paraffin and rectified bone oil with lithium into strong-walled pure iron tubes, which he heated to red heat for about 14 hr. The "diamonds" he produced were kept for many years in the British Museum, and were investigated crystallographically by PROFESSOR KATHLEEN LONSDALE and her collaborators in 1943. They were shown to be true diamonds of a very rare transparent variety, so whether HANNAY actually produced diamonds is still a matter for debate. SIR CHARLES PARSONS also tried, for 30 years, to synthesise diamonds—including the duplication of MOISSAN'S and HANNAY'S experiments—but never successfully.

The carbon phase diagram (Fig. 2) shows that diamond is the stable form at ordinary temperatures at pressures as low as 15,000 atm., but all attempts to produce diamonds at room temperatures, even at pressures as high as 400,000 atm., have failed, as the transition rate is extremely slow. At temperatures of the order of 2000°C the transition rate is much faster, but the transition pressure is also increased to about 100,000 atm. Nevertheless, using such conditions for periods of several hours, a team in the General Electric Research Laboratories in Schenectady succeeded in making diamonds about 1 mm long.[5] These workers have also made another "industrial diamond", "Borazon", a compound of boron and nitrogen, using similar temperatures but somewhat lower pressures. Subsequently, the Swedish ASEA also reported successful diamond synthesis, using temperatures of 2700°C with pressures of 85,000 atm.

In these two articles (Parts 1 and 2) it has only been possible to give a brief account of some specific chemical effects of pressure, but not of the underlying physical principles which explain many of them. An excellent account of these, and a much fuller discussion than has been given here, can be found in the recently published "Physico-chemical Effects of Pressure", which has frequently been referred to.

The interest in high pressure is growing, and many other aspects of the subject which we have not been able to cover in these articles are currently being investigated. These include developments of high-pressure pumping and compression machinery and heat transfer at high pressures.

ACKNOWLEDGEMENTS

The author is indebted to his former colleagues at the C.S.I.R.O. High Pressure Laboratory, University of Sydney, and especially DR. S. D. HAMANN, the head of the laboratory.

REFERENCES

[1] Weale, K. E. *Disc. Faraday Soc.*, 1956, **22**, 122.
[2] Hamann, S. D. *Disc. Faraday Soc.*, 1956, **22**, 144.
[3] Hamann, S. D. "Physico-chemical Effects of Pressure", Butterworths Scientific Publications, London, 1957, p. 192.
[4] Perrin, M. W. *Research*, 1953, **6**, 111.
[5] Bundy, F. P., Hall, H. T., Strong, H. M., and Wentorf, R. H. *Nature*, 1955, **176**, 51.
[6] Hamann, S. D., and Teplitzky, D. R. *Disc. Faraday Soc.*, 1956, **22**, 114.
[7] David, H. G., and Hamann, S. D. *Trans. Faraday Soc.*, 1954, **50**, 1188.
[8] Nicholson, A. E., and Norrish, R. G. W. *Disc. Faraday Soc.*, 1956, **22**, 97.

BIBLIOGRAPHY

Hamann, S. D. "Physico-chemical Effects of Pressure" (Butterworths), 1957.
Faraday Society Discussion No. 22, "The Physical Chemistry of Processes at High Pressure" (Glasgow, 1956).
Strauss, W., Univ. Sheffield, *Fuel Society Journal*, 1957, **8**, 69-87.

66.096.5: 537.226: 539.217.1

POROSITY DETERMINATION OF FLUIDISED BEDS

The evolution of a relation between dielectric constant and the porosity of mixtures of glass spheres and air

by Dr. Ir. P. J. BAKKER and Prof. Dr. Ir. P. M. HEERTJES

MEASUREMENTS on the porosity distribution in a fluidised bed consisting of glass spheres and air have been carried out with the aid of a small condenser immersed in the fluidised bed.[1] To translate the measured capacity (linear proportional to the dielectric constant of the mixture between the plates of the condenser) into a porosity-value, a relation between the porosity and the dielectric constant of the mixture as measured had to be determined. This article will deal with the evaluation of the method used for the determination of this relation.

The capacity, C, of a condenser with rectangular parallel plates is given by:

$$C = \frac{Do \,.\, D \,.\, S}{4\,\pi\,d} \qquad \ldots . (1)$$

where C = capacity of the condenser;
Do = constant, depending on the chosen system of units;
D = dielectric constant of the medium between the plates of the condenser;
S = surface area of plates; and
d = distance apart of plates.

The dielectric constant, D, of a mixture depends on the dielectric constants, on the relative volumes and for heterogeneous mixtures, such as that considered, on the mutual orientation of the constituents.

A relation between the dielectric constant of a mixture of gas and solids and those of the constituting gas and solid substance is relatively simple for two limiting geometrical configurations. If the solid phase should form one compact mass on the upper side of the condenser, as given in Fig. 1, two parallel condensers are present, for which:

$$C_{total} = C_{glass} + C_{air} \qquad \ldots . (2)$$

If the solid phase forms a compact mass as given in Fig. 2, two condensers in series are present, for which:

$$1/C_{total} = 1/C_{glass} + 1/C_{air} \qquad \ldots (3)$$

By substituting Equation (1) in the Equations (2) and (3) and realising that ϵ = volume air/(volume air + volume glass), the following expressions can be derived:

$$D = (1 - \epsilon).D_1 + \epsilon.D_2 \qquad \ldots (4)$$

(parallel condensers)

and $$1/D = (1 - \epsilon)/D_1 + \epsilon/D_2 \qquad \ldots . (5)$$

(condensers in series)

Symbols Used

C = capacity of a condenser, pF;
C_{air} = capacity of a condenser, containing air as medium, pF;
C_{glass} = capacity of a condenser, containing glass as medium, pF;
C_{total} = capacity of a condenser, containing air and glass as medium, pF;
D_o = constant, Coulomb^2 sec.^{2}/kg m^3;
D = dielectric constant, dimensionless;
D_1 = dielectric constant of the discontinuous medium, dimensionless;
D_2 = dielectric constant of the continuous medium, dimensionless;
$D_{0.4}$ = dielectric constant of a mixture of glass spheres and a continuous medium with a porosity of 0.40, dimensionless;
D_{l+s} = dielectric constant of a mixture of liquid and solids, dimensionless;
D_l = dielectric constant of a liquid, dimensionless;
d = distance of condenser plates, m;
S = surface of condenser plates, m^2;
T = temperature, °C; and
ϵ = porosity, dimensionless.

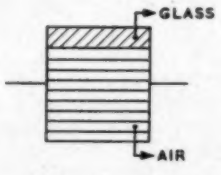


FIG. 1

ONE LIMITING GEOMETRICAL SITUATION, SOLID PHASE FORMS A COMPACT MASS ON THE UPPER SIDE OF THE CONDENSER.

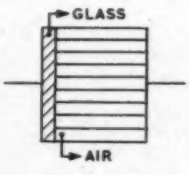


FIG. 2

THE OTHER LIMITING CONDITION, SOLID PHASE FORMS A COMPACT MASS ON ONE PLATE OF THE CONDENSER.

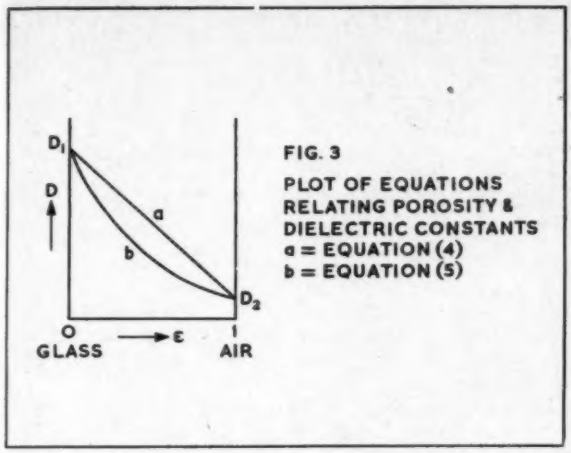


FIG. 3
PLOT OF EQUATIONS RELATING POROSITY & DIELECTRIC CONSTANTS
a = EQUATION (4)
b = EQUATION (5)

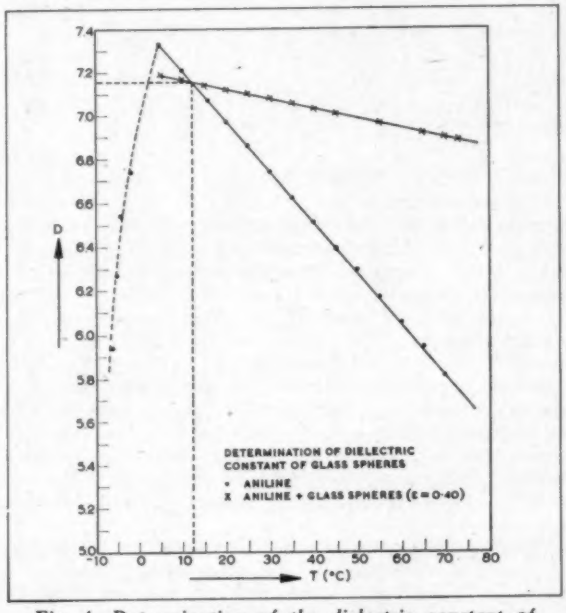


Fig. 4. Determination of the dielectric constant of glass spheres (first method).

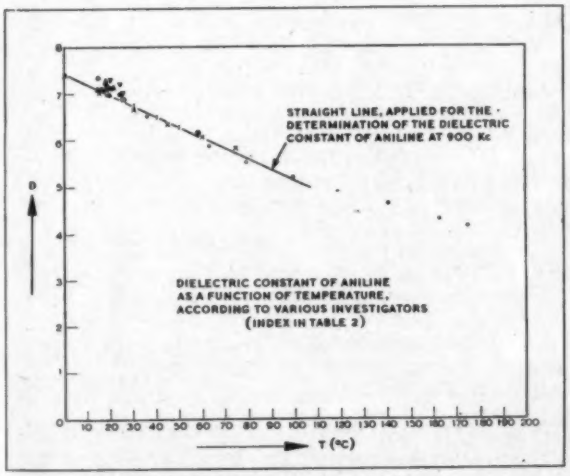

STRAIGHT LINE, APPLIED FOR THE DETERMINATION OF THE DIELECTRIC CONSTANT OF ANILINE AT 900 Kc
D
DIELECTRIC CONSTANT OF ANILINE AS A FUNCTION OF TEMPERATURE, ACCORDING TO VARIOUS INVESTIGATORS (INDEX IN TABLE 2)
T (°C)

Fig. 5. Dielectric constant of aniline versus temperature.

The indexes 1 and 2 refer respectively to glass and air; ϵ is the porosity of the mixture. Fig. 3 gives a graphical presentation of Equations (4) and (5).

It will be clear that for a random configuration of glass spheres in air, neither line *a* nor line *b* in Fig. 3 expresses the actual D-ϵ function, which will lie in between, depending on the mutual orientation of the two phases.

Many equations have been presented in the literature with regard to the relation of D and ϵ for isotropic mixtures in which the solids are homogeneously divided in the gas. This literature is reviewed in the next section.

Literature on Dielectric Constant-Porosity Relations

Several authors have tried to give a theoretical or an experimental solution of the relation between the dielectric constant and the porosity of isotropic mixtures of solids and gases. The presented results, however, are in such disagreement that no justified choice as to the relation to be used in the present case can be reached. This will be clear if the following review of equations valid for spherical solids suspended in a continuous medium is considered. The equations given will be presented without discussion as to their derivation or to their merits.

RAYLEIGH[3] has initiated the mathematical basis for the theoretical approach of the problem in question. The relation of RAYLEIGH for the dielectric constant D of the mixture, the porosity ϵ of the mixture and the dielectric constants D_1 or D_2 of the discontinuous and the continuous phase is:

$$D = D_2\left[1-(1-\varepsilon)\frac{3}{\frac{2\,D_2+D_1}{D_2-D_1}+(1-\varepsilon)-1,65.\frac{D_2-D_1}{4/3\,D_2+D_1}.(1-\varepsilon)^{10/3}}\right] \quad \ldots.(6)$$

RAYLEIGH restricted the validity of this equation to high porosity-values. A very extensive and thorough study of the problem by WIENER[3] has led to the following function:

$$\frac{D-D_2}{D+2D_2} = (1-\varepsilon).\frac{D_1-D_2}{D_1+2D_2} \quad \ldots.(7)$$

An exponential equation resulted from the work of LICHTENECKER[4]:

$$D = D_1^{(1-\epsilon)}.D_2^{\epsilon} \quad \ldots.(8)$$

while BRUGGEMAN,[5] after many experiments, concluded that:

$$\varepsilon = \frac{D_1-D}{D_1-D_2}\sqrt[3]{\frac{D_2}{D}} \quad \ldots.(9)$$

WACHHOLTZ and FRANCESON,[6] in verifying the above-mentioned equations, could not find agreement with their results and suggested a new relation:

$$D = \frac{D_2\left\{1+\frac{D_2-D_1}{D_1}-(1-\varepsilon)^{\frac{1}{3}}.\frac{D_2-D_1}{D_1}\right\}}{1+\frac{D_2-D_1}{D_1}-(1-\varepsilon)^{\frac{1}{3}}.\frac{D_2-D_1}{D_1}+(1-\varepsilon).\frac{D_2-D_1}{D_1}} \quad \ldots.(10)$$

For spherical particles in air ($D_2=1$), BÖTTCHER[7, 8] developed:

$$\frac{D-1}{3D} = (1-\varepsilon).\frac{D_1-1}{D_1+2D} \quad \ldots.(11)$$

According to GUILLIEN,[9] the LICHTENECKER equation gave the best results, provided that the ratio D_1/D_2 did not differ very much from unity. It will be understood that in such a case the physical difference between the two media becomes small and that for such a case each relation should give a reasonable approach.

TABLE 1

Temperature (°C)	Dielectric constant of aniline	Dielectric constant of aniline + glass spheres
− 6	5.94	—
− 5	6.27	—
− 4	6.54	—
− 3	6.64	—
− 1.5	6.74	—
5	7.33	7.19
10	7.21	7.17
15	—	7.14
16	7.07	—
20	6.96	7.12
25	6.86	7.10
30	6.74	7.08
35	6.62	7.06
40	6.51	7.03
45	6.39	7.01
50	6.29	—
55	6.17	6.97
60	6.05	—
65	5.94	6.92
70	5.81	6.90
73	—	6.89

TABLE 2

Symbol in Fig. 5	Author	Literature Ref.	Temp. (°C)	Freq. (Kc)	D
⌈x	Ratz	13	0	0	7.42
.	Jezewski	14	0.25	600	7.42
Δ	Drude	15	14	4.10^5	7.14
o	Jahn and Möller	16	14.3	0	7.36
x	Ratz	13	15	0	7.03
o	Jahn and Möller	16	16	0	7.12
■	Nenst	17	17.5	0	7.24
▲	Turner	18	18	0	7.31
Δ	Drude	15	18	4.10^5	7.15
.	Jezewski	14	18.4	600	6.98
⊗	Schlundt	19	18.5	4.10^5	7.2
▽	Dobroserdov	20	19.3	4.10^5	7.3
■	Nernst	17	20	0	7.14
′	Estermann	21	20	1000	6.98
Δ	Drude	15	21	4.10^5	7.15
■	Nernst	17	24	0	7.01
▼	Mathews	22	24	4.10^5	7.2
□	Lunt and Rau	23	25	900	6.90
⌣	Clay *et al.*	24	25	1000	6.99
–	Joachim	25	25	1000	7.05
x	Ratz	13	30	0	6.68
′	Estermann	21	30	1000	6.75
.	Jezewski	14	35.7	600	6.53
′	Estermann	21	40	1000	6.52
x	Ratz	13	45	0	6.37
′	Estermann	21	50	1000	6.29
◐	Kerr	26	58	3000	6.20
x	Ratz	13	60	0	6.09
.	Jezewski	14	63	600	5.87
x	Ratz	13	75	0	5.86
.	Jezewski	14	79	600	5.56
.	Jezewski	14	99	600	5.22
.	Jezewski	14	118	600	4.94
.	Jezewski	14	140	600	4.67
.	Jezewski	14	162	600	4.33
.	Jezewski	14	174.5	600	4.19
⌒	Grimm and Patrick	27	184.55 (Bp.)	—	4.54

JOTTRAND[10] examined the equations of RAYLEIGH, WIENER, LICHTENECKER, BRUGGEMAN and WACHHOLTZ and FRANCESON, but could not find a satisfactory agreement for his own experiments on liquids and solids.

Finally, the work of HOUGH and REYNOLDS[11] and of DE LOOR[12] should be mentioned. These authors again could not find agreement between their experiments and the equations as presented. DE LOOR even states that for each system an experimental relation should be determined, especially if the particles are irregular in shape.

The above will have made it clear that so far neither a theoretical nor an experimental relation between D, ϵ, D_1 and D_2 has been found which is applicable to every mixture of spherical particles and a fluid. Therefore, a direct experimental approach of the relation between the dielectric constant and the porosity for the system investigated has been preferred.

Isotropic suspensions of glass spheres in air are rather difficult to form. It has therefore been undertaken to measure the relation of D, ϵ for systems of liquids and glass spheres, in which case the right choice of the density of substances permits the realisation of isotropic suspensions. From these measurements a relation has been derived. This relation has been checked as to its applicability on mixtures of glass spheres and air on a few selected points and has proved to be successful.

The Dielectric Constant of Glass Spheres

The first method adopted for the measurement of the dielectric constant of the glass spheres consisted of determining the dielectric constant-temperature relation of a liquid over a range including the dielectric constant of glass and of a mixture of the liquid with the solids. Since the temperature-coefficient of the dielectric constant of solids is much smaller than those of liquids, the curves obtained will intersect. This point of intersection is the dielectric constant of the solid at the temperature of intersection. Because the temperature-coefficient of the dielectric constant of glass is small compared with the accuracy needed, this value will be taken as the dielectric constant of glass. Aniline carefully purified by distillation and crystallisation has been used as the calibration liquid for the glass spheres.

The measurement of the dielectric constant of the liquid or the liquid-solid mixture takes place with a condenser, immersed in the system. The condenser consists of three flat copper plates of 1 cm² surface; both the external plates are earthed, the inner plate carries the voltage. By means of a coaxial cable, the condenser is connected with the capacity measuring apparatus. The capacity has been measured by means of a Wheatstone's bridge. For a full description of the apparatus see Reference [1].

The temperature range used was from −6 to +75°C. The mixture of the glass spheres and aniline formed a fixed bed of solids in liquid with a porosity $\epsilon = 0.40$. It appeared that both the temperature coefficients of the dielectric constants of the aniline and of the mixture were constant above 5°C. The results are given in Table 1 and Fig. 4.

The intersection could be easily determined; a value of 7.16 ± 0.01 at 12°C has been found.

In order to translate the measured values—meter indication—into a dielectric constant, use has been made of values derived from the literature of the dielectric constant of aniline, measured at various temperatures and frequencies, of which a survey is given in Table 2 and Fig. 5.

From Fig. 5 it can be seen that the value of the dielectric constant is dependent on the frequency of the method used (see also LUNT and RAU[23] and JOACHIM[25]).

Considering Fig. 5, a rather large spread in the values

is observed. On the one side this is caused by the large differences in the frequencies applied; on the other hand differences can certainly be caused by more or less severe impurities in the aniline used. LUNT and RAU[23] have carried out a determination at 25°C and 900 Kc; the experiments mentioned in this article have been carried out at the same frequency.

Since from the experiments a constant temperature coefficient of the meter indication, and therefore of the dielectric constant of aniline, has been found, from the most accurate literature values, measured at an almost identical frequency (~ 900 Kc) a linear correlation with temperature was established and used as a calibration line (line in Fig. 5) for translating meter values into dielectric constants. No absolute dielectric constants are obtained this way. However, it may be stated that no absolute determination of dielectric constants was intended; only a value of the order of magnitude of the dielectric constant was wanted, with which all meter values could be compared.

A second method for measuring the dielectric constant of glass spheres consists of the determination of the difference in dielectric constant of a liquid and a mixture of glass spheres and the same liquid at one temperature for liquids with a range of dielectric constants covering the dielectric constant of the glass spheres. Here, again, fixed beds of glass spheres and liquids of a constant porosity ($\epsilon = 0.40$) have been used. If there is a large difference between the dielectric constants of liquid and glass spheres, the increment between the dielectric constants of liquid and mixture will be directly proportional to this difference. Fig. 6 shows a graphical correlation of these increments against the dielectric constants of the liquids used. The dielectric constant of the solid is equal to the dielectric constant of that liquid for which the increment becomes zero.

This method has the advantage of the use of one frequency and of one temperature. Translation of the measured values into dielectric constants takes place using the relation obtained before. The above method has been carried out with 25 liquids. The results are given in Table 3 and Fig. 6.

According to this method, a dielectric constant of the glass spheres of 7.15 ± 0.02 has been found.

Relation of ϵ and D for an Isotropic Mixture of Glass Spheres and a Liquid

For the determination of the ϵ-D function as noted above, homogeneous suspensions of glass spheres and liquids had to be produced. For this, a liquid is needed with a density approximately equal to that of glass spheres and, moreover, for extrapolation to systems with air instead of a liquid, preferably one with a dielectric constant as close as possible to the dielectric constant of air. A suitable liquid meeting these demands is bromoform with a density of 2.84 at 20°C (the density of glass spheres is 2.84) and a dielectric constant of 3.97 at 20°C and 900 Kc (dielectric constant of air = 1). Isotropic suspensions of glass spheres and bromoform with known porosities can now easily be produced by stirring the mixture of the components. A minimum porosity of $\epsilon = 0.40$ can be reached; in the range of $\epsilon = 0.40$ to $\epsilon = 1$ measurements can be carried out. Table 4 and Fig. 7 give the results.

For comparison both the functions of Fig. 3 have been inserted in Table 4 and Fig. 7.

It appeared that the D-ϵ relation determined showed a good agreement only with the WIENER equation, which is also represented in Table 4 and Fig. 7. Only at low ϵ-values is there a small deviation. This is probably caused by drift of the measuring apparatus. It may be concluded that for the system bromoform-glass spheres the equation of WIENER can be applied.

TABLE 3

Liquid	D_l	D_{l+s}	$D_{l+s}-D_l$	
Pentane	1.27	3.55	2.28	
Cyclohexane	1.45	3.80	2.35	
Carbontetrachloride	2.08	4.49	2.41	
Toluene	2.09	4.54	2.45	
Benzene	2.15	4.47	2.32	
O-Xylene	2.40	4.75	2.35	
Trichloroethylene	3.07	5.07	2.00	
Bromoform	3.97	5.75	1.78	
Chloroform	4.51	5.98	1.47	Frequency: 900 Kc
Diethylether	4.54	5.93	1.39	
Dimethylaniline	4.75	6.07	1.32	
Bromobenzene	5.19	6.25	1.06	Temperature 20°C
Chlorobenzene	5.44	6.38	0.94	
Ethylacetate	5.97	6.60	0.63	
Benzyl chloride	6.42	6.74	0.32	
Methyliodide	6.63	6.95	0.32	
Methylacetate	6.92	7.13	0.21	
Aniline	6.97	7.12	0.15	
Allylchloride	7.48	7.27	− 0.21	
Ethylbromide	9.54	8.08	− 1.46	
Mixtures of ethylbromide and paraldehyde	9.61	8.14	− 1.47	
	9.93	8.27	− 1.66	
	10.42	8.48	− 1.94	
	12.26	9.08	− 3.18	
Paraldehyde	13.60	9.40	− 4.20	

(D_l: dielectric constant of the liquid;
D_{l+s}: dielectric constant of a mixture of liquid and glass spheres.)

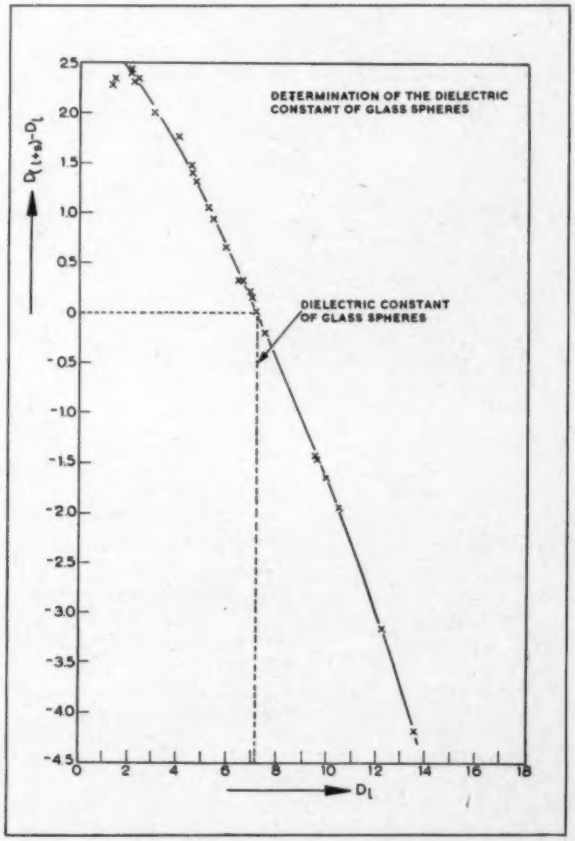


Fig. 6. Determination of the dielectric constant of glass spheres (second method).

TABLE 4

ε	*D* linear function	*D* calculated (WIENER)	*D* hyperbolic function	ε measure-ments	*D* measure-ments
0	7.15	7.15	7.15	0.40	5.75
0.1	6.83	6.77	6.62	0.418	5.70
0.2	6.51	6.38	6.17	0.436	5.64
0.3	6.19	6.03	5.77	0.457	5.56
0.4	5.88	5.70	5.42	0.480	5.48
0.5	5.56	5.36	5.11	0.504	5.41
0.6	5.24	5.06	4.84	0.532	5.29
0.7	4.92	4.78	4.58	0.564	5.21
0.8	4.61	4.49	4.36	0.598	5.11
0.9	4.29	4.23	4.16	0.626	4.99
1.0	3.97	3.97	3.97	0.657	4.90
				0.692	4.80
				0.729	4.70
Temperature: 20°C				0.772	4.57
				0.822	4.43
				0.877	4.31
Frequency: 900 Kc				0.943	4.11
				1.000	3.97

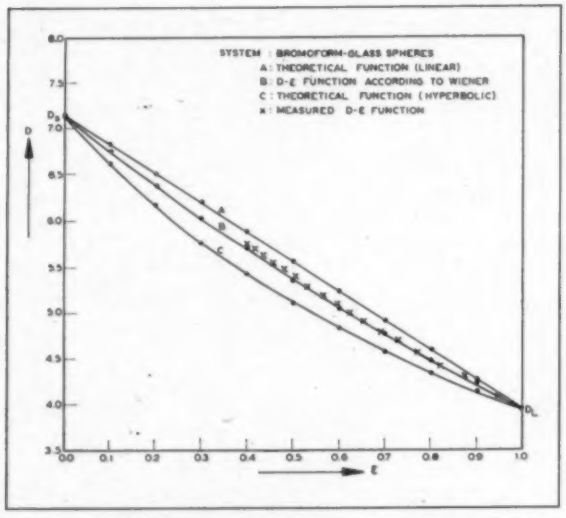

SYSTEM : BROMOFORM-GLASS SPHERES
A : THEORETICAL FUNCTION (LINEAR)
B : D-ε FUNCTION ACCORDING TO WIENER
C : THEORETICAL FUNCTION (HYPERBOLIC)
x : MEASURED D-ε FUNCTION
D
ε

Fig. 7. Dielectric constant versus porosity for the system bromoform-glass spheres.

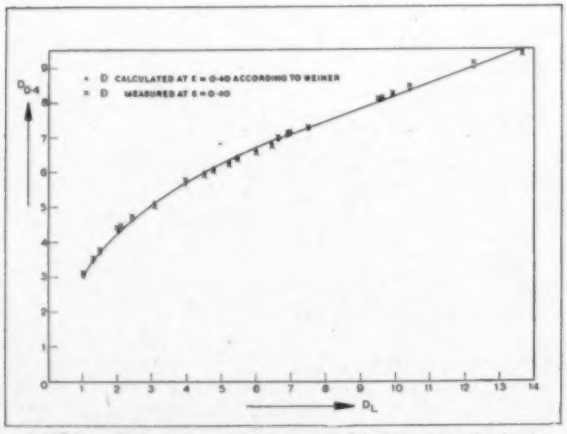


Fig. 8. Dielectric constant of a fixed bed of glass spheres and a liquid versus dielectric constant of the liquid.

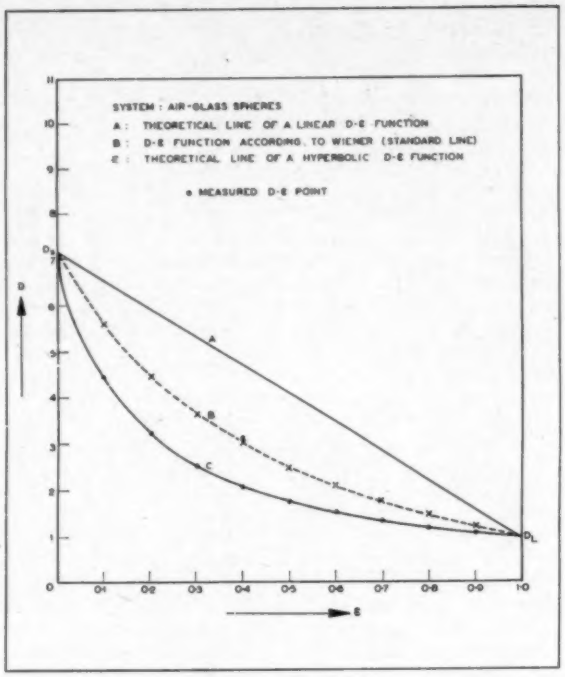

SYSTEM : AIR-GLASS SPHERES
A : THEORETICAL LINE OF A LINEAR D-ε FUNCTION
B : D-ε FUNCTION ACCORDING TO WIENER (STANDARD LINE)
C : THEORETICAL LINE OF A HYPERBOLIC D-ε FUNCTION
MEASURED D-ε POINT
D
ε

Fig. 9. Dielectric constant versus porosity for the system air-glass spheres.

TABLE 5

Liquid	*Dl*	$D_{0\cdot4}$ (WIENER)	$D_{0\cdot4}$ (measured)	Deviation	% Deviation
Pentane	1.27	3.45	3.55	+ 0.10	+ 2.8
Cyclohexane	1.45	3.70	3.80	+ 0.10	+ 2.6
Carbon tetrachloride	2.08	4.38	4.49	+ 0.11	+ 2.5
Toluene	2.09	4.39	4.54	+ 0.15	+ 3.2
Benzene	2.15	4.45	4.47	+ 0.02	+ 0.45
O-Xylene	2.40	4.66	4.75	+ 0.09	+ 1.9
Trichloroethylene	3.07	5.15	5.07	− 0.08	− 1.6
Bromoform	3.97	5.70	5.75	+ 0.05	+ 1.0
Chloroform	4.51	5.98	5.98	0	0
Diethylether	4.54	6.00	5.93	− 0.07	− 1.2
Dimethylaniline	4.75	6.11	6.07	− 0.04	− 0.7
Bromobenzene	5.19	6.31	6.25	− 0.06	− 1.0
Chlorobenzene	5.44	6.42	6.38	− 0.04	− 0.6
Ethylacetate	5.97	6.66	6.60	− 0.06	− 0.9
Benzyl chloride	6.42	6.85	6.74	− 0.11	− 1.6
Methyliodide	6.63	6.94	6.95	+ 0.01	+ 0.1
Methylacetate	6.92	7.06	7.13	+ 0.07	+ 1.0
Aniline	6.97	7.08	7.12	+ 0.04	+ 0.6
Allylchloride	7.48	7.29	7.27	− 0.02	− 0.3
Ethylbromide	9.54	8.06	8.08	+ 0.02	+ 0.2
Mixtures of ethylbromide and paraldehyde	9.61	8.09	8.14	+ 0.05	+ 0.6
	9.93	8.20	8.27	+ 0.07	+ 0.8
	10.42	8.37	8.48	+ 0.11	+ 1.3
	12.26	9.02	9.08	+ 0.06	+ 0.7
Paraldehyde	13.60	9.47	9.40	− 0.07	− 0.7
				average:	+ 0.4

($D_{0\cdot4}$: dielectric constant of a liquid-glass spheres mixture with a porosity of 0.40.)

Application of the Wiener Equation to Various Liquid-Glass Spheres Mixtures

It is important to know whether the WIENER equation also holds for other liquid-glass spheres mixtures. Experimentally, this question can only be answered incompletely, since for other liquids the demand for identical or nearly identical densities of the constituents of the mixture will in most cases not be fulfilled and the achievement of isotropic suspensions will be rather difficult. However, it has been found that fixed beds of glass spheres and these liquids have a porosity of ~ 0.40 in all cases. These beds can be formed and the dielectric constants can be measured quite reproducibly. For a variety of liquids these measured dielectric constants have been compared with those calculated with the aid of the WIENER equation. The values obtained have been given in Table 5.

The differences in measured and calculated values are small, considering the possible errors in the measurements; furthermore, the differences are alternately positive and negative, with a mean deviation of $+0.4\%$.

In Fig. 8 the measured (crossed) and calculated (circles and drawn line) dielectric constants of the liquid-glass spheres mixtures are given as a function of the dielectric constants of the liquids used; the measured values fit very well within the curve. It can be concluded that the WIENER equation is valid for the liquid-glass spheres systems, independent of the fact whether the dielectric constant of the liquid is larger or smaller than the dielectric constant of the glass spheres.

Relation between D and ε for the System Air-Glass Spheres

From the validity of the WIENER equation for mixtures of glass spheres and liquids, including liquids approaching the dielectric constant of air, it can be assumed that the D-ε relation for isotropic mixtures of air and glass spheres can also be represented by the WIENER equation, since from a physical point of view no difference exists between a liquid and a gas as the continuous medium in a condenser field. A direct proof can only be obtained with certainty for a bed which has just previously been fluidised (which has a porosity $\varepsilon = 0.40$). The calculated value for such a bed according to WIENER is 3.03. Experimentally a value of 3.09 has been found. It can therefore be concluded that for the system of air-glass spheres the WIENER equation can be used to express the ε-D relation. In Table 6 and graphically in Fig. 9 this relation has been presented. For the range $\varepsilon = 0.40$ to $\varepsilon = 1.0$ the WIENER line can now be used as a calibration line for transferring measured capacities (i.e., dielectric constants) into porosities.

The procedure as described in this article can be applied to other systems as well, provided that the porosities of the mixture and the dielectric constants of the constituents are known. The method described can be a tool for other investigations in which dielectric constants have to be measured.

TABLE 6

ε	D linear function	D calculated according to WIENER	D hyperbolic function
0	7.15	7.15	7.15
0.1	6.53	5.60	4.46
0.2	5.92	4.48	3.23
0.3	5.30	3.66	2.53
0.4	4.69	3.03*	2.06
0.5	4.07	2.52	1.75
0.6	3.46	2.10	1.52
0.7	2.84	1.76	1.34
0.8	2.23	1.46	1.21
0.9	1.61	1.21	1.09
1.0	1,00	1.00	1.00

*Measured value: 3.09

Conclusion

For isotropic mixtures of glass spheres and air the relation between the porosity (ε) and the dielectric constant (D) of the mixture can be expressed by the equation of WIENER, which has the form:

$$\frac{D-D_2}{D+2D_2} = (1-\varepsilon)\,\frac{D_1-D_2}{D_1+2D_2}$$

in which D_1 is the dielectric constant of glass, D_2 that of air.

REFERENCES

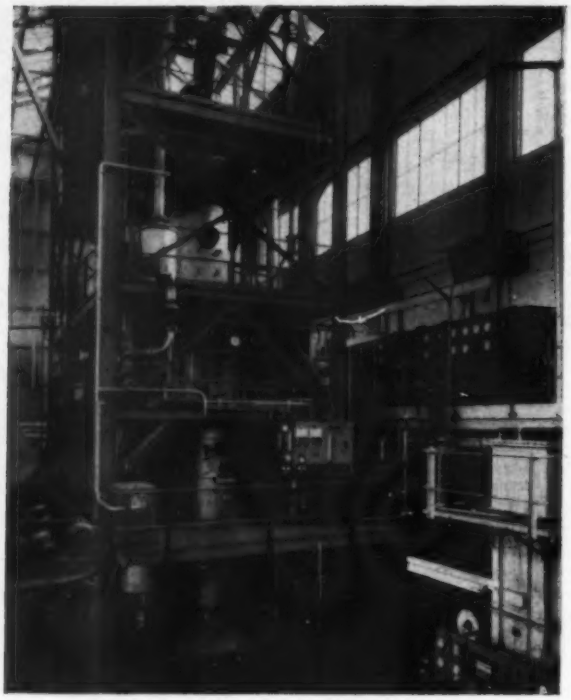
[1] Bakker, P. J., and Heertjes, P. M. *Brit. Chem. Eng.*, 1958, **3**, 240.
[2] Rayleigh, J. W. *Phil. Mag.*, 1892, **34**, 481.
[3] Wiener, O. *Abhandl. Sächs. Ges. Wiss. Math. Phys. Kl.*, 1912, **32**, 509.
[4] Lichtenecker, K. *Physik. Z.*, 1918, **19**, 374.
[5] Bruggeman, D. A. G. *Ann. Physik.*, 1935, **24**, F.5 636.
[6] Wachholtz, F., and Franceson, A. *Kolloid Z.*, 1940, **92**, 75.
[7] Böttcher, C. J. F. Theory of electric polarisation. Els. Publ. Cy. A'dam 1952.
[8] Böttcher, C. J. F. *Rec. trav. chim.*, 1945, **64**, 47.
[9] Guillien, R. *Ann. Phys.* (Paris), 11e série, 1941, no. 16, 205.
[10] Jottrand, R. *Chem. Eng. Sci.*, 1951, **1**, 81.
[11] Hough, J. M., and Reynolds, J. A. *Arch. Sci.* (Genève) 1956, **9**, 34.
[12] De Loor, G. P. Thesis Leiden 1956.
[13] Ratz, F. *Z. physik. Chemie*, 1896, **19**, 94.
[14] Jezewski, M. *J. Phys. Radium*, 1922, **3**, 293.
[15] Drude, P. *Z. physik. Chemie*, 1897, **23**, 267.
[16] Jahn, H., and Möller, G. *Z. physik. Chemie*, 1894, **13**, 385.
[17] Nernst, W. *Z. physik. Chemie*, 1894, **14**, 622.
[18] Turner, B. B. *Z. physik. Chemie*, 1900, **35**, 385.
[19] Schlundt, H. *J. Phys. Chem.*, 1901, **5**, 503.
[20] Dobroserdov, D. *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1385.
[21] Estermann, I. *Z. physik. Chemie*, 1928, **B 1**, 134.
[22] Mathews, J. H. *J. Phys. Chem.*, 1905, **9**, 641.
[23] Lunt, W. R., and Rau, M. A. G. *Proc. Roy. Soc.*, London, 1930, A **126**, 213.
[24] Clay, J., *et al. Physica*, 1943, **10**, 768.
[25] Joachim, H. *Ann. Physik.*, 1919, **60**, 670.
[26] Kerr, R. N. *Phil. Mag.*, 1927, **3**, 330.
[27] Grimm, F. V., and Patrick, W. A. *J. Am. Chem. Soc.*, 1923, **45**, 2794.

A Film of Catalytic Reforming*

In essence, the whole story of a platformer catalytic reforming unit is ably presented in these two new instructional films. Part 1 largely treats the basic chemistry of the changes, while Part 2 takes the viewer around the working unit. Why is naphtha unsuitable for use as a motor fuel? Its composition—mainly normal paraffin molecules—is indicated and the need to produce a fuel containing more compact aromatics. The reforming reactions—shown by the skilled use of all modern artifices—are the aromatising of normal paraffins, isomerisation of iso-paraffins, hydro-cracking to smaller molecules and desulphurisation. On this groundwork the second part dealing with the unit builds up a full diagram of each section.

Part 1 won the Premier Award in the category Education and Training within Industry at the 1959 Harrogate Festival of Films in the Service of Industry. Part 2 well matches it in quality. There were only minor flaws. It did not seem reasonable that such a tangible object as a compressor, shown diagrammatically, should be still when the invisible hydrogen passing through it is depicted as beginning to flow. Representation of heat exchangers did not seem satisfactory in failing to show streams maintained mechanically separate, although brought into close thermal contact. Yet these are minor adverse notes. The films are successful and could help anywhere in the training of personnel where comparable processing is being carried out. I.B.

* *Catalytic Reforming*. Part 1—The Reforming Reaction. 13 minutes Sound, colour. Gt. Britain, 1958. Part 2—The Reforming Unit. 14 minutes. Sound, colour. Gt. Britain, 1959. Both produced by Merton Park Productions in association with the Film Producers' Guild for British Petroleum. Available from the Petroleum Films Bureau, 29 New Bond Street, London, W.1.



66.013.5

SPECULATIVE PILOT DESIGN AND SCALE-UP — PART I

Is it possible to reduce or eliminate research for scale-up of plant? The author develops his thesis of postulating a mechanism

by Dr. DONALD Q. KERN

THE decision to abandon a plant-design research project several years after its initiation confronts the research director with one of his unpleasantest responsibilities. In this article a speculative approach to engineering research is proposed to reduce the incidence of such project closures. It is *inexact* and employs certain informalities and liberties during the research programme which should be admissible under the scientific method, although they currently enjoy relatively little popularity.

Cheaper, Surer Research

A speculative approach differs from conventional concepts in that *it does not have precision as its early objective*, but only eventually achieves it when it proves necessary—and then only sparingly. It is a mathematical procedure which devoutly employs experimentation for the purpose of confirming mechanisms rather than the wholesale production of tabulated numbers and *a posteriori* conclusions.

The credit aspects of a speculative approach lie in the assurance they provide that a plant-design research project will get off to a sound start at a *lower cost* rather than provide a precise answer later. After all, it doesn't really matter how precisely an answer is obtained if it proves to have no further application.

More important, it is often possible to determine without much outlay whether a programme is worth starting at all. Everything is focused at the outset on the two principal nemeses of every project; running out of funds, and/or running out of reportable technical progress.

The first essential step may be called *reverse thinking*. Consideration is not given for the small-scale plant from which data will evolve for the design of a large-scale plant. Instead, the interest is in the design of a large-scale plant at the outset and only those small-scale experiments are designed which can be used on the large scale. In practice, this produces many broad gaps which must be plugged. But it eliminates the preference for performing easier experiments rather than useful ones.

The continuity of efforts outlined here originated from first-hand reviews of a number of experimental thermal research programmes which declined from the pinnacle of hope to the threshold of abandonment. A few of many rescued projects are included in the illustrative examples.

There are a number of useful empirical tools which facilitate the collection of the greatest amount of process plant design knowledge from a limited amount of experimentation. Recent articles appearing in *Chemical Engineering*[1] and texts[2, 3] have directed attention to the merits of similarity criteria. This is an excellent recommendation, but it concentrates attention on the act of correlation rather than the appraisal of the basic novelty of a physical or chemical system, or the need for the experiments and the competence of their design.

The Speculative Approach

There is much to be learned about a physical or chemical change simply through a postulation of the mechanisms possible within it by mathematical analysis and particularly differential equations. For example, it is known that under certain conditions electrical systems and hydraulic systems obey analogous differential equations. Why not carry out the required experiments confidently in the more convenient system?

The diffusion of matter and conduction heat transfer are also described by similar characteristic equations. Mechanisms provide by far the most unlimited opportunities for confident chemical plant scale-up. However, before borrowing differential equations, it must be established that they also obey the same boundary conditions before they qualify as analogues.

Occasionally there is difficulty identifying any mechan-

ism at all and it is necessary to speculate from scratch. There is no need under these circumstances for even a precise starting speculation. In fact, it is often advisable to throw in a few extraneous factors which should be self-liquidating when hypothetical boundary conditions are imposed.

It is not intended here to offer apologies for the speculative approach because of the small premium it places on early precision or the possibility that it will promote a new low in sloppy research. It will develop a cost-conscious research which endeavours to obtain an answer which is only as good as required—and no better. The requirement keeps changing as the project continues.

From this point of view precision is very often undesirable—particularly when it becomes a fetish. At the start of a project it rapidly consumes funds and slows progress with irrelevant considerations for such things as reproduceability, calibration and deviation when the only thought should be: "Can it be made to work?" This represents a separation between the qualitative and quantitative research phases—and before it arises the principal effort should be mental rather than physical.

A professional designer of plants will not use experimental information without some personal adjustment. To make a tenfold or twentyfold scale-up he will not employ similarity ratios of 10:1 or 20:1. Most likely the design of the prototype plant will include a 20% to 50% margin. The designer's only concern is that he is providing the fat where he believes it is. For this type of design he only requires an indication rather than a collection of highly refined and costly data.

Since it is rarely possible to preserve all aspects of similarity in a plant of moderate complexity during scale-up, the need for precise small-scale data is further reduced. Precision on the small scale may very well lose its significance as soon as scale-up is undertaken. In some instances it may be unique only to the small scale. Conceivably, the design sequence from pilot to prototype may even eliminate the need for highly calibrated measurements at any stage of development.

Unfortunately, there are many blind spots in the speculative postulation of a mechanism by differential equations—some of the common equations lack straightforward solution and this leaves no other course but short-range empiricism. All roads lead toward empiricism and it will be shown later that even here differential equations provide many of the avenues themselves.

Short-range empiricism, in its lower forms, merely produces a point per run on some sort of graph, or another entry in a table. These appear to be short odds for a large investment, since they shed little light, if any, on mechanism, a point so essential to the design of large plants from small ones. All signposts point to the *a priori* approach for clicking off the most miles per unit of cost.

The Case for Similarity Theory

Through the speculative postulation of mechanism it is often possible to reduce the research time requirements significantly. It would be unwise, however, to overlook the advantages which are contained in the simpler aspects of similarity theory, even when unassisted by differential equations.

In the case of ultimate simplicity, similarity theory only requires the assembly of one bench or pilot-scale component of a process, rather than an entire process, and the performance of a single experiment. This would occur when it is desired to build a component just like the pilot plant with respect to perhaps a single index of similarity, say geometrical similarity.

Because of fabricating limitations, not all components can be scaled-up economically while preserving similarity, nor would this be desirable from the standpoint of plant layout. When additional indices of similarity are superimposed, such as mechanical, kinematic and thermodynamic similarity it may also be impossible to scale-up because of inconsistencies in the demands of the different criteria.

When it appears that too little is known about a system to warrant scale-up on the basis of similarity the situation obviously requires a probe. It is not possible to conduct an intelligent quantitative measurement of all significant effects without knowing what to look for beforehand or to what extent the instruments should be calibrated.

A probe is the identification of response variables such as properties, temperature, pressure, surface, etc. These should preferably be carried out inexpensively on a tiny bench scale. The tests require little or no precision and often a qualitative response is enough. Compare all of the responses obtained with a catalogue of the variables of other systems containing the same variables, plus others, to observe whether a test or property may have been omitted. This is easily done with punched cards and may be the first step toward determining that the probe system and other systems may indeed possess important mechanism similarities which were not previously apparent. It is then possible to proceed with similarity techniques.

FROUDE[4] is generally conceded to have established the first milestone in mechanical similarity and hence in isothermal process scale-up technique. By drawing a model of a ship's hull across the free surface of a test basin at a given velocity, data were obtained which were successfully used for the design of large ocean-going vessels.

The next important development followed within a few years, when REYNOLDS[5] investigated streamline flow in closed, full-flowing conduits. Both FROUDE and REYNOLDS were able to establish criteria of similarity by noting that in both systems the ratio of inertial force to the frictional force acting on an element of fluid was everywhere constant. In Froude's case the resistance force was due to the gravitational pull on the hull. The ratio of the two forces in Froude's case is defined by

$$\frac{\text{Inertial force}}{\text{Gravity force}} = \text{constant} = \frac{\rho V^2/L}{\rho g} = \frac{V^2}{gL} \quad \ldots.(1)$$

L is an arbitrary length dimension, and the last term is generally referred to as the Froude number, N_{Fr}.

In the analysis of REYNOLDS the system was considered to have no free surface, so that the action of gravity was nullified by buoyant equality. The ratio of the two forces for this case is

$$\frac{\text{Inertial force}}{\text{Frictional force}} = \text{constant} = \frac{\rho V^2/L}{\mu V/L^2} = \frac{\rho VL}{\mu} \quad \ldots.(2)$$

The last term in the equation is the familiar REYNOLDS number, N_{Re}.

Thus the REYNOLDS number, although dimensionless, describes a ratio of forces in a system of forces without defining the actual value of either force. A system of dimensionless ratios or groups may frequently be obtained very simply compared with a mathematical analysis which would be obliged to treat the absolute order of magnitude of both of the forces. For this reason, the handling of dimensionless groups has been collected into an area of analysis called the *theory of similarity*.

Dimensionless groups and *dimensional analysis* should not be confused. The resolution of effects into dimensionless groups places the matter on a basis of ratios which are independent of the size of the system. Dimensional analysis is simply one of several algebraic techniques for manipulating the dimensions of variables so as to achieve dimensionless groups.

By means of the theory of similarity one may obtain from the tiny bench-scale probe those independent variables which appear capable of causing a response in a dependent variable. It is then possible to arrange all of the variables into dimensionless groups as described heretofore. The experimenter can now operate upon these groups by either of two methods, depending upon the number of constants he may be willing to evaluate by experiment. The simpler method is called *theory of models*.

The theory of models states that if a general relationship exists between a single dimensionless group N_1 and other dimensionless groups such as N_2, N_3, $N_4 \ldots N_n$, so that

$$N_1 = f(N_2,\ N_3,\ N_4 \ldots N_n) \qquad \ldots . (3)$$

then N_1 must be fixed by the numerical values of N_2, etc., taken in any manner and regardless of the form of the function f.

When it is desired to determine N_1 for a large-scale process, one may do so simply by establishing a model or pilot plant in which all of the groups on the right side of Equation (3) bear the same numerical relationship with each other as those in the large-scale plant. This procedure accordingly requires a single test and gives but a single value for N_1.

The theory of models commends itself by its simplicity. Its great short-coming is that it never identifies the function f and hence identifies neither the mechanism nor the relative contribution of the individual variables which one may wish to change from time to time. This is a great limitation in the development of quantitative design information.

Rarely does one want to design an industrial plant which will obviously look like an overgrown pilot plant and possess all of its limitations. In an industrial plant greater funds will be available to incorporate many elements of design which will give the production plant greater operating economy and permanence. This means that, in numerous respects, it will not be desirable to have the prototype follow the model too closely. Variations will be introduced at the industrial design level which perhaps cannot be studied in the model.

The second approach under the theory of similarity is a refinement of the theory of models by employing a function f in the form of a *power series*. If a dependent variable is expressed in terms of its independent variables, the independent variables can be arranged in a succession of dimensionless groups which simulate the pure magnitude of a group containing the dependent variable. This requires the evaluation of one or more additional constants for each term in the series until the desired experimental deviation is reached. The pilot plant required for this kind of information may differ considerably from the one tested by the theory of models.

Such a pilot plant will allow for the handling and measurement of changes in the variables and the programme of experiments will be longer of necessity, but this may be inconsequential beside the original cost of assembling the pilot plant. The exponential values of the variables in each of the dimensionless groups obtained by dimensional analysis will also be indicated.

This means of pre-analysis is of great importance in the calibration of the measurements by which the variables in a group will be observed and can lead to the accumulation of relatively good design data from a limited number of experiments. For example, if one variable influences a group to the $4n$ power and another to the $n/4$ power, and the exponent of the group is greater than zero, the end result will be only about as good as the ability to calibrate the variable with the $4n$ exponent. In this form similarity theory cannot tell why an independent variable influences a result, but it can give an excellent indication of how much it influences it.

The power series approach has one very great limitation. It is essentially a tool for interpolation only. Suppose one is to design a large plant engaging a large group of measured variables over a very wide operating range. It may be too costly to reproduce the entire range of variables in the pilot, although they may be economically available in the proposed large-scale plant. In order to become familiarised with the contributions of the individual variables and the dimensionless groups into which they may be resolved, a range of experimental variation must be established.

There is also a matter of data displacement which is incidental to the use of plant-design data. Research results are usually correlated in terms of the mean with a notation relative to the mean deviation of the data. The mean is of little value in design, since the curve or equation so obtained must be juggled upward to provide a measure of assurance that all or most of the deviations are negative. It is not the desire to learn on the large scale whether or not a plant will work but rather to make certain that it will. The curve-juggling phase may prove to be the most important step in the entire scale-up sequence.

The true function may pass through a maximum. The range of experiment, however, may only encompass the ascending or descending slope of a two-dimensional curve. By producing a graph with a small average deviation in some co-ordinate system, the impression may be compelled that one is measuring a straight-line function in the co-ordinate system.

When the pilot-plant data are extrapolated to the industrial scale, it is possible that data have been used in which the inversion at the maximum was never approached—and the extrapolated plant actually might never work. There are a number of instances of just this kind of thing[6]—the scaled-up commercial plant that laid an egg because it could not be scaled-up retaining all criteria of similarity and could not produce the rated capacity with the proposed investment and operating costs.

The Case for Mathematical Analysis

Mathematical analysis should first serve as the "dry run" in proposing a mechanism for the system. Mechanisms, we note, are the things which can be scaled-up quite freely. It should be determined whether or not there is really something new to be learned through experiment or whether a programme will merely reconfirm with a new assembly of hardware, and another fluid, a type of response which is already well known. The postulation should rest upon the relatively invariant laws of physics and chemistry and often will be amenable to computer simulation. Never hesitate to borrow data on analogous systems from the literature.

It is surprising to observe that when real boundary conditions are imposed upon the postulation, however abstruse the mechanism may be, much information may be revealed. It may be revealed, for example, that a great increase in the only variable directly commensurate with operating cost cannot materially increase the yield of a chemical reaction or the efficiency of a mechanical system. If increased yield or efficiency is the principal objective of the programme, one would best abandon further thoughts about constructing a pilot.

The postulation will also contain *all* of the pertinent measurable quantities, along with a suggestion of their relative calibration. This is also a logical separation between the quantitative and qualitative phases of the programme. While dimensional analysis can assist with the calibration of the variables to be measured, it does

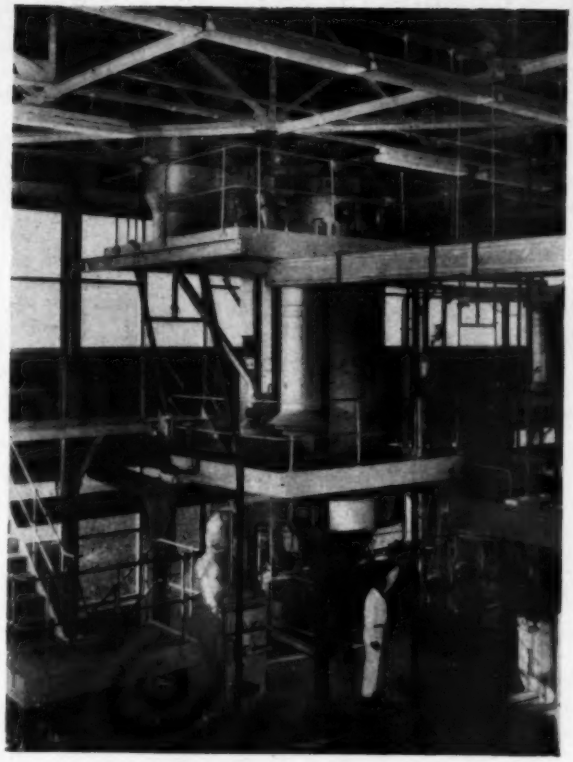


Fig. 2. Miniature spray drying tower for washing powders. (Photo: Thomas Hedley & Co. Ltd.)

not reveal what variables *must* be measured. Dimensional analysis only offers the prospect through a probe of identifying all the significant variables.

It is often pointed out that one can proceed through dimensional analysis when only a partial picture of the system has been obtained. This is not a virtue. Partial identification only produces a partial result, which, contrarily, can be much worse than no result at all. For the scale-up of chemical processes, a relatively small number of mathematically definable chemical and physical processes need to be considered. The basic equations for these processes are known and, if these equations could be rigorously solved, the scale-up problem would be essentially non-existent.

The scale-up problem does exist, however, for three reasons: (1) Many of the important basic equations are unsolvable by known general mathematical techniques. (2) The basic phenomena are often interconnected; that is, the basic equations are coupled. The coupling relations are not always known, may obscure each other, and, in any case, increase the mathematical difficulties. (3) The necessary physical data for a solution are frequently unknown and there is some belief that pilot-plant data, particularly in chemical kinetics, are better than bench-scale data.

A catalogue of the common thermal process operations is contained in the Appendix along with their equations and comments on the method of solution.

Consider now how these equations can be converted to dimensionless form using Equation (X) in the Appendix

$$c_p\rho\frac{\partial t}{\partial\theta} = \left[\frac{\partial}{\partial x}\left(k_x\frac{\partial t}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y\frac{\partial t}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z\frac{\partial t}{\partial z}\right)\right] - c_p\rho\left(u\frac{\partial t}{\partial x} + v\frac{\partial t}{\partial y} + w\frac{\partial t}{\partial z}\right) + G$$

as an example for a system having no internal heat generation. The first term is the rate of net enthalpy change, the second is the rate of change by conduction and the third is the rate of change by convection. Writing these in dimensional form and dividing the first and last terms by the dimensions of the second term results in an expression in terms of the NUSSELT and PECLET numbers; thus

$$\varphi\left(\frac{hD}{k}, \frac{c_pDV\rho}{k}\right) = \text{Const.} \qquad \ldots.(4)$$

Multiplying the numerator and denominator of the PECLET number by the viscosity μ leads to the familiar result

$$\varphi\left(\frac{hD}{k}, \frac{DV\rho}{\mu}, \frac{cp\mu}{k}\right) = \text{Const.} \qquad \ldots.(5)$$

Solution of Postulated Equations

In any given problem involving differential equations, it is also necessary to define the boundary conditions. These are fixed by the nature of the problem (e.g., zero velocity at the wall in a flowing fluid) and may be themselves non-linear.

A number of mathematical tools of varying degrees of rigour are available. For straightforward rigorous solution, it is usually necessary that the equation or equations and initial and boundary conditions be linear. When non-linear equations of necessity must be substituted into non-linear equations it is better to change some premises or resort to numerical methods. There is little chance of going far unless some type of convergence is in sight.

A number of methods are available for solution of second-order partial differential linear equations of the general form

$$\nabla^2\varphi + f = \alpha\frac{\partial^2\varphi}{\partial\theta^2} + \beta\frac{\partial\varphi}{\partial\theta} \qquad \ldots.(6)$$

where φ = dependent variable;
∇^2 = Laplacian operator;
f = function of position;
θ = time; and
α, β = specified physical constants.

Many of the more important equations encountered in engineering problems can be obtained by specialising the above form. For example, Fourier's equation, Equation (IX) of the Appendix, for constant physical properties

$$cp\rho\frac{\partial t}{\partial\theta} = \frac{\partial}{\partial x}\left(kx\frac{\partial t}{\partial x}\right) + \frac{\partial}{\partial y}\left(k_y\frac{\partial t}{\partial y}\right) + \frac{\partial}{\partial z}\left(k_z\frac{\partial t}{\partial z}\right) + G$$

is obtained if

$\varphi = t$, temperature;
$f = G/k$;
G = internal heat generation rate;
k = thermal conductivity;
$\alpha = 0$;
$\beta = \rho c_p/k$;
ρ = density; and
c_p = specific heat.

Quasi-linear problems have also received some attention resulting in some fairly general techniques.

Many, but not all, of the solution methods require separability; that is, reduction of the partial differential equation to a set of ordinary differential equations. The choice of method of solution depends upon the particular form of the equation, system symmetry, and the nature of the boundary conditions. Representative methods are:

Series solutions
Bessel functions
Legendre polynomials
Hypergeometric functions
Fourier series

Integral transforms
Laplace transform
Fourier transform
Method of characteristics
Conformal mapping

If the original equation or set of equations cannot be solved, several paths are available depending upon the problem and the type of knowledge desired:

(1) Frequently, the problem itself can be simplified without great loss of accuracy, and a rigorous solution obtained for the simplified model. An excellent example is the reduction of the NAVIER-STOKES equations by boundary layer theory.
(2) Sometimes the equations can be linearised by judicious approximation, as typified by OSEEN'S treatment of the NAVIER-STOKES equations. Often, however, such techniques only slightly extend the applicability of even more reduced forms of the general equations.
(3) Almost any system of equations can be solved by numerical analysis, using machines. Specific solutions only are obtained, and the solution for a number of different sets of values may become costly. Monte-carlo methods may be especially applicable to problems involving kinetics and/or diffusion.
(4) Analogue solutions, either by electronic analogue computers or more specialised apparatus such as conducting paper, conducting solutions, or stretched membranes can be obtained for a variety of problems, especially those involving transients.
(5) Analogy relationships, as between momentum-, heat- and mass-transfer, commend the application of existing data on one system to another.
(6) Reduction of the general equations to dimensionless parameters indicates the important groupings of the variables involved and the terms of the equation in which they appear, and aids in the proper application of bench and/or pilot-plant data.
(7) Finally, the equations themselves may indicate important features of the solutions, even though the solutions are never obtained. This method requires considerable mathematical insight.

Frequently, two or more of the above techniques can be combined for greater effectiveness. For example, one might combine an approximate analytical solution near the surface and a numerical calculation in the core of a hot rectangular metal bar being quenched. Example 1* under illustrative examples is of this type.

Attention should be paid to the possibility of replacing difficult or non-linear boundary conditions by more amenable forms. Linear equations with linear boundary conditions have the property that solutions are additive or "superposable"; it is possible in this way to solve a number of relatively simple problems and combine the solutions into that for a complex problem.

It is sometimes possible to solve two simple problems whose solutions are known to bracket that of the desired but more complex problem. Example 2† is of this form. From this the desired solution may be satisfactorily estimated, or it may be enough to know the bounds of the solution.

Derivative Experimentation

The use of differential equations naturally confronts one with the evaluation of derivatives. Common procedures all too often lead to the measurement of variables which are usually integrals, such as a distance, or a weight change, or a time interval rather than the direct measurement of a derivative such as the velocity.

The measured integrals may contribute different relative precisions and include sequential observations even when measured automatically; that is, it may be necessary to measure the flow and temperature changes in a stream at three or more different places. The observations may be simultaneous at the various places, but the stream may undergo fluctuation throughout the distance over which the points are deployed. This is particularly true of unsteady state measurements.

Suppose it is desired to measure the average fluid velocity in a conduit. This can be accomplished by allowing fluid to flow into a can over a measured time interval and measuring the weight or volume or effluent. These are all integrals. However, it may be possible to measure the velocity instantaneously through the use of some invariant physical law.

POISEUILLE has shown that a proportionality exists between the velocity of the fluid and fluid friction. Suspend an object in the flowing stream and measure the resistance the object affords the flow of fluid. The frictional force can be transferred to a linear measurement through the displacement of a spring suspending the object as indicated on a piece of graph paper.

Instrument manufacturers frequently use this procedure, but what does it mean? By reading the displacement of the spring one is continuously identifying the term $\partial x/\partial \theta$ when all other influencing variables are held constant. Even if the device were originally calibrated through the measurement of integral properties, it is nevertheless a device for measuring a first-order derivative directly.

Assume next that the rate of flow of the fluid varies such that it continuously increases, decreases or alternately does both. By observing the displacement of the spring on a constantly moving graph, it is possible to measure the second-order derivative $\partial^2 x/\partial \theta^2$ continuously and instantaneously without integrals.

* Example 1 (to be given in Part II) deals with the expanding of a non-theoretical equation for the film heat transfer coefficient in a scraped surface heat exchanger.
† This example deals with the development of a probe for a thin film process.

(To be continued)

Electronic Computer in Commerce

SHOTS of a boisterous market-place form the opening sequence of a film for senior and middle executives produced by Unilever Ltd. with the title *The Electronic Computer in Commerce*. More staidly, the film—expanded from one intended to accompany the last Faraday lecture—goes on to show how these machines can help in organising business on a larger scale.

Introducing a computer can often speed up routine clerical work and suggest new forms of improved administrative control. But first there must be an analysis of the existing procedure. How an existing clerical system is analysed into its components is shown in this film with an illustration from the work of a records clerk. A typical clerical operation can usually be analysed into five stages—input, storage, control, calculation and output.

But apart from payroll type of applications, the film refers to possible uses in devising the best buying programme, choosing best sources of raw materials or arranging the cheapest combination of transport routes. The material is excellently presented except for the omission of a worked example. The impact would have been greatly increased if a case study had been shown carried to its final conclusion, showing a rearrangement of buying procedure or transport organisation due to information quickly processed and presented by this device. With this limitation, however, the film generally fulfils its purpose.

66.01: 061.3

AN INTERNATIONAL CONFERENCE ON CHEMICAL ENGINEERING*

A summary of papers covering a broad spectrum

Action of steam at high temperature on lean fluorspars; thermal extraction of fluorspars in the form of hydrofluoric acid, by J. Chastel.

HYDROFLUORIC acid is usually prepared from fluorspars by reaction with sulphuric acid. This procedure presumes that there are rich minerals available or that one can easily enrich to 98-99% of CaF_2 eliminating in particular silica because each atom of silicon degrades six atoms of fluorine in the form of H_2SiF_6. The process presented by the author was intended for lean minerals, siliceous by preference, which are not economically capable of being worked by any concentration procedure. The principle consists of reacting steam at high temperature with the mineral which has previously been molten with the addition of products necessary for the formation of a convenient slag.

The thermokinetic elements of the following overall reactions have been taken into consideration

$$SiO_2 + CaF_2 + H_2O \xrightarrow[1250°C]{} CaSiO_3 + 2\,HF - 44{,}000 \text{ kcal.}$$

The Nernst formula gives the order of magnitude of the equilibrium constant

$$K_P = \frac{P^2_{HF}}{P_{H_2O}} = \text{approx. } 200$$

The parasitic reaction $SiO_2 + 4HF \leftarrow SiF_4 + 2\,H_2O$ causes practically no trouble for at 1300°C the equilibrium $H_2O/HF/SiF_4$ is such that there is less than 1% of SiF_4 in the gas.

For application of this process it was decided to bring the steam and the cast slag into contact in an electric furnace. This technique made it necessary to determine in advance the physical properties necessary for carrying out the operations such as the fusion point, viscosity and the electrical resistivity of the mixtures. The yields in the form of gaseous HF are of the order of 75%. The energy consumption is of the order of 11,000-12,000 kcal/kg HF.

Ion exchange as a chemical engineering operation, by M. M. David.

ION exchange has today become an industrially important operation, but methods of design of the industrial installations have only just begun to develop compared with those which exist for the other fundamental operations of chemical engineering. The structure of ionic exchangers and the mechanism of ion exchange are well described in the technical literature and it is only necessary to recall them briefly.

Industrially the ion exchanger is generally arranged in a fixed bed through which there flows a continuous current of fluid. There are available mathematical analyses of the behaviour of a fixed bed and the paper discussed the current limitations and the future possibilities of the method. It then went on to summarise the other methods employed for specifying the dimensions and operating conditions of an industrial unit, describing the various factors which influence the economic study of the process.

Ion exchangers are also employed in the form of distinct batches, which may be operated continuously or discontinuously or also in counter-current continuous systems. It was shown that the calculations of these different methods of working are identical to those which are developed for other comparable fundamental operations, such as distillation, liquid-liquid extraction and absorption. There was also reference to new uses of ionic exchangers in the form of both membranes permeable to ions and those impermeable to ions.

The movement of electricity accompanying the movement of liquids and its consequences. The electricity called static, by A. Klinkenberg.

THE movement of electrically insulating liquids can give rise to electric charges in these liquids themselves and in surrounding objects. Very intense fields can result from this. As is known, in the petrol industry current methods such as the earthing of reservoirs are insufficient or even quite inadequate to eliminate the danger of explosion. A fundamental study was therefore necessary in order to improve the knowledge of the mechanisms of the generation, accumulation and dissipation of the charges.

The author considered the transport of electricity according to the methods of chemical engineering and compared it with other transport phenomena well known to chemical engineers such as that of heat and of non-charged matter. He showed how the differences between the movement of heat or of non-charged matter and that of the charged ions are based on characteristic differences of the fundamental equations, and examined the consequences.

As examples of the generation of electricity he considered the movement in pipes and in the sedimentation of a water/liquid hydrocarbon emulsion—both of these being of practical importance.

Experimental difficulties in the application of the so-called two film absorption theory, for the drying of air by sulphuric acid, by S. Hardouin.

PUBLICATIONS devoted to the study of absorption columns make it seem possible to define the dimensions and the operating conditions of an industrial packed

* Journées Européennes du Génie Chimique, XX° Manifestation de la Fédération Européenne du Génie Chimique.

absorption column by means of a simple preliminary determination in the laboratory. The only experimental part of the study necessary for carrying out the calculations consists in measuring the value of a specific coefficient for the relevant operation. This coefficient may be the overall mass transfer coefficient of the liquid and gas films—determined by means of a standard film column—or it may be the height equivalent to a mass transfer unit for the packing chosen, determined by means of an element of absorption column of small diameter.

In fact the application of these methods for the design of industrial columns is limited by the difficulties met in trying to determine the values of the basic coefficients. Furthermore, the determination of the other elements necessary for the calculation such as the specific surface of the packing, the number of transfer units and the absorption potential quite often result in approximations. It is often necessary to have recourse to industrial experimentation in order to check the data drawn from laboratory experiments; at the same time it is necessary to confirm the applicability of the method.

A practical example concerning the study of the drying of air by sulphuric acid in a packed column made it possible to put the emphasis on the experimental difficulties which result on the one hand from material contingencies and on the other from the limitations of the means of control. The field of application of the conventional methods of calculation is still very limited but it is possible to envisage a rapid extension in the future.

Contribution to the control of the flow of fluid in a reactor, by R. Drouhin.

CERTAIN reactions between gases require the reactants to be introduced into a large capacity vessel constituting the true reactor. The control of the paths and the expansion of the gaseous streams as soon as they leave the nozzles may therefore be necessary. This result can only partially be attained by the design of the nozzle and it is therefore interesting to return to the properties of the jets to maintain control over the flow of the stream without having recourse to other methods.

With this in view, experiments have been made with some success on enveloping the principal gaseous stream by a fluid film issuing from a secondary circuit. In another series of trials it has been possible to a certain extent to control the enveloped form of the stream without a secondary fluid circuit but by the application of properties known under the name of induced draught: a deflector slightly narrows the stream a little above the nozzle which increases its speed and creates a slight depression under the deflector; the stream then draws into the limited space in which it flows the fluid which envelops it.

Such experiments are essentially of interest for confirming the value of recourse to experiment in matters of fluid mechanics applied to problems of chemical engineering; in this field, in fact, each problem appears as a particular case so that the application of the general ideas demands the sanction of experience.

Evaluation of the efficiency of liquid-liquid extraction columns, by A. Vignes and P. Le Goff.

THE evaluation of the efficiency of an extraction column operating continuously, by the height equivalent to one transfer unit, HTU conforms more closely to the transfer process than the evaluation by means of height equivalent of a theoretical plate, HETP.

The authors, therefore, decided to make a critical study of the method of calculation based on height of a transfer unit. They showed that the generalised use of diffusion equations to express the transfer velocity between phases in the column is justified if one can define a mean contact time between phases along the column. Also they found that the equations established on the basis of this hypothesis are equally valuable without it being necessary to introduce supplementary hypotheses of inter-facial equilibrium, of a permanent transfer régime and of the non-miscibility of the solvent and diluent.

Kinetics of crushing, by M. Patat.

AFTER a review of the tests carried out so far by Gundermann, Hüttig and his collaborators, the author analysed the phenomena of crushing in ball mills and showed that for "differential crushing" only, it is possible to establish expressions for the kinetics of size reduction. Thermodynamic relationships have not been established.

For differential crushing the speed of pulverising can be represented as a function of the parameters of the crusher —volume, diameter and weight of balls, rotational speed, temperature—by a simple differential equation.

$$dG/dt = k \cdot G^n$$

dG/dt represents the speed with which a determined fraction of particles G is powdered, k is a constant and n the order of the crushing process. The application of kinetics and the description of the crushing phenomena by means of constants are justified and explained by 3000 tests carried out with dry sand of different size ranges and at different temperatures.

Kinetic analysis makes it possible for the first time to obtain an indication of the consistency of the powder and of complexity of the crushing action. Finally, the author shows the advantages which can result from applying the speed of crushing as a characteristic property of a substance to the problems of size distribution analysis.

Experimental determination of liquid-vapour equilibria, by Louis Kaiser.

THIS paper gave a general view presenting the various principles on which ebulliometers and tonometers are based in order to derive the precision and ease with which the variables of the liquid-vapour equation state can be determined. These principles were represented by models of which the most significant were distinguished, on the one hand by very simple apparatus of adequate precision sometimes based on the cyclic principle, sometimes on the flow principle, and on the other hand by more complex models which attained great precision based on the static or the dynamic principle.

For the models of the second type, the experimental data agreed very well and it was difficult to decide among the stationary states interpreted by these data which was the nearest to complete equilibrium.

Percolation through a fixed adsorbent bed, by Jean Desseine.

THE difficulties encountered on trying to find the composition of the adsorbant phase and the lack of direct correspondence between the compositions of the two phases considerably complicates analysis of adsorption on a fixed bed in the liquid phase. The theoretical plate concept has been proposed by different authors to take account of the resistances to attainment of equilibrium. In this paper the author uses a plate concept analogous to a perfect mixing tank. In the particular case of elution of a band by a non-adsorbable solvent with a linear equilibrium isotherm, it is found that the calculations and the results are analogous to those proposed by Mayer and

Tompkins for the analysis of ionic exchange phenomena.

The comparison of theoretical results with experiments in the case of percolating the mixtures cyclohexane-benzene and water-tertiary butyl-alcohol on active carbon shows that the number of plates in a column decreases as the adsorbent approaches saturation.

Choice between air and water cooling, by L. Guilleaux.

WITH liquids that are not very viscous, economic studies show that the combination of water cooling preceded by air cooling can be more economical than the use of water cooling alone. As the viscosity increases the transfer coefficient of the air coolant decreases faster than that of the water coolant which favours the use of the latter rather than the former up to the limit where air cooling is completely abandoned in the case of viscous liquids.

Treatment of water for cooling towers, by J. Delaunay

THE aim of this paper was to follow the different stages which marked the evolution of the treatment of water in the water recirculating circuits at Port-Jérôme up to the point where a balance was attained among scaling, corrosion of the circuits and conservation of the wood of the towers. The treatment adopted consists of a light decarbonation followed by sequestration by polyphosphates. The results obtained were very satisfactory.

Use of tracers in industrial research, by P. V. Danckwerts.

TRACERS can be used to obtain information on the path of products in manufacturing installations or other systems. By appropriate tests it is possible to determine the general flow characteristics (for example complete mixture, homogeneous stream, short circuiting etc.). Equally one can determine the quantity of product in a system and its rate of flow when these cannot be directly measured. Exploration of the interior of a system by tracers gives information on stagnant regions, reverse flow and so on.

Outside of chemical engineering the process finds application in the study of ventilation, water flow across reservoirs or underground, discharge of drainage to the sea and so on.

Rectification in an empty column, by H. Brusset.

THE study of the mass exchange surface between the liquid and the gaseous phase in distillation is facilitated by considering the case of an empty rectification column. It is experimentally observed that the efficiency of a rectification column decreases with the diameter and with the rate of flow of the fluids. The variation of efficiency presents two distinct forms according to whether the régime of flow is linear or turbulent. The influence of the composition is not negligible at large rates of flow. The results are capable of analysis by means of the film theory which makes it possible to represent them by an expression for efficiency as a function of the column diameter, the Reynolds and Schmidt Numbers for a single determined mean composition of rectification. It is still necessary to explain the change of form of the efficiency curves close to the critical Reynolds number. Optical observation shows the existence of cavities in the contact surface of the two phases. The frequency of these deformations can be the basis of an interpretation.

Research on the optimum conditions for extractive distillation, by L. Le Bec and P. Le Goff.

EXTRACTIVE distillation is an operation which utilises the fact that the relative volatility of the constituents of a binary mixture can be profoundly modified by the presence of a third much less volatile substance. The essential features of this operation were defined and the types of mixtures where separation by distillation can be facilitated by this artifice. The choice of a third substance can be guided by thermodynamic considerations (evaluation of activity coefficients) or structural ones (polarity and molecular association) but the final choice involves experimental determination of liquid-vapour equilibria. The industrial techniques and published results were then briefly discussed. Methods of calculation for fractionating columns were derived from those used for ordinary ternary mixtures. Abbreviated methods of calculation were presented. The distribution of the third substance along the fractionating column was studied and the validity of the approximations used in calculation. The authors showed the necessity for carrying out further theoretical and experimental researches and described an installation at Nancy for carrying out industrial tests under continuous flow conditions.

Statistical study of small particles, by F. Vergnes.

MACROSCOPIC populations have their characteristics generally described by the normal law of Gauss; on the molecular or atomic scale, the Maxwell distribution gives a good representation of the phenomena. In the intermediate domain which is fundamental for several industries (crushing, fixed bed or fluidised catalysis, filtration, decantation, etc.) which is that of small particles, the problem is infinitely less simple. The case of particles obeying a Gaussian distribution is rather rare: it occurs with substances produced by a physico-chemical process such as condensation or precipitation. Nevertheless, we should attempt to describe mathematically other distributions. Two ways are open: (a) to find another form of distribution such as that of Rosin-Rammler, (b) to find a simple function of the size of the particle which follows a Gauss distribution. The usual method for doing this is the Kapteyn transformation and its particular case, which is the most usual, the log-normal law which can be applied quite well to the products of a crusher. In practice the use of papers constructed according to the Galton curve makes it possible to determine quickly the parameters which define normal and log-normal distributions.

Characterisation of catalysers and of chemical reactions, by H. I. Waterman.

IT has been proved that in many cases it is possible to characterise chemical reactions and in general catalytic chemical processes by means of hyperbolae. This method uses the well-known graphical representation of the mixtures concerned by a right-angle triangle having equal sides. The corners of the triangle a, b and c represent for example the first material a, the desirable products of reaction b, and the undesirable products c. Each point in the triangle represents the composition of a reaction product. It is particularly reactions having a selective character which can be represented in this triangle. Naturally there are limits to the use of this system and these were discussed. Nevertheless, it has been possible to characterise not only chemical transformations but also to find the characteristics of the catalysers which are linked with the system studied. Thus one can equally easily study the influence of certain factors on the process for example, pressure, temperature, contact time and so on. The system can be applied to a great number of varied reactions such as hydrogenation, isomerisation, cracking, oxidation, chlorination and so on. It makes it possible to limit the number of experiments particularly when working on continuous processes.

621.039.431:662.73

FISSION PRODUCT WASTE FROM REACTORS —PROCESSING OF HIGHLY ACTIVE SOLUTIONS

Increasing use of atomic energy means a growing problem of waste disposal. Types of active wastes and methods of treating them are reviewed in this article by a research worker at A.E.R.E., Harwell

by T. V. HEALY, M.Sc., A.R.I.C.

As more and more experience is forthcoming in dealing with atomic waste products, we can clearly discern the pattern of the underlying principles that will eventually govern such operations. In the case of large and concentrated radioactivities, there is a tendency towards complete containment, preferably without losing control of the products; in the case of comparatively small and dilute activities, the tendency is towards complete dispersal, so that the concentration of radioactive products falls well below the limits of tolerance.

These principles are modified by the practical considerations of the desirable degree of processing to which these waste products can be subjected. In the case of dilute waste, for example, "processing" may separate out a large fraction of activity in small bulk, which can be "contained", while the remainder goes towards dispersal, which now becomes either cheaper or safer. In the case of concentrated fission products, "processing" may lead to a volume reduction, or towards making the material safer to handle, or towards separating the waste products into a small volume of long-lived material to be "contained" and a large volume of short-lived and inactive bulk which may be "dispersed" at some later date.

The latter approach receives special encouragement from the fact that the long-lived isotopes (in the main, Sr and Cs) represent not only the greatest danger in any waste disposal scheme, but are at the same time most valuable if used in concentrated form as sources of radiation—for medical, research or industrial processes. It is on this last theme, a combined programme of industrial utilisation and disposal, that we wish to give more detailed technical information.

Types of Highly Active Waste

The choice of technical operations which can be applied usefully depends both on the type and composition of the fuel element used and on the chemical procedure which has been applied for the separation of the fission products from the nuclear fuel to be recycled.

Types of Fuel Element

The table below gives examples of different types of fuel element in some present-day reactors.

Reactor	Fuel Type
BEPO and Windscale Piles (U.K.) NRX (Canada) ZOE (France), SLEEP (Sweden) Russian Power Reactor (U.S.S.R.) BNL Graphite Reactor (U.S.A.)	Uranium metal clad in aluminium
CP 2 Chicago (U.S.A.)	Uranium plus UO_2
Saclay (France)	Uranium metal clad in magnesium
Hanford Reactors (U.S.A.)	Aluminium jacketed uranium (probably bonded)
MTR, TTR and ORNL (U.S.A.)	UAl_4 bonded in Al
Los Alamos Fast Reactor (U.S.A.)	Pure plutonium clad in mild steel.

Types of Waste Solutions

Several methods of processing fuel elements have been reported.[1] Nitric acid dissolution has been used for uranium, uranium-aluminium alloy and thorium, and could be used for plutonium-aluminium alloy. Sodium hydroxide has been considered for dissolution of aluminium jackets, uranium-aluminium alloy and partially for plutonium-aluminium alloy. Aluminium jackets have also been removed mechanically. Elements containing zirconium can be dissolved in HF.

American Redox Process

Uranium plus aluminium fuels are dissolved in nitric acid to produce an acid-deficient system, that is, a system containing less nitrate ions than corresponds to the stoichiometric requirements of aluminium nitrate and uranyl nitrate. With the aid of the aluminium as a salting-out agent, good separation of plutonium and uranium is effected by solvent extraction with hexone or TBP, leaving a 0.2 molar acid-deficient aqueous fission product solution of high aluminium content.

British Dibutyl Carbitol Process

After irradiation and "cooling", the aluminium jackets are cut away from the uranium metal which is dissolved in nitric acid to give an acid solution of uranium, plutonium and fission products. On extraction with dibutyl

Mr. Healy, *a Principal Scientific Officer at Harwell, has been actively concerned for some years with the separation and purification of fission products.*

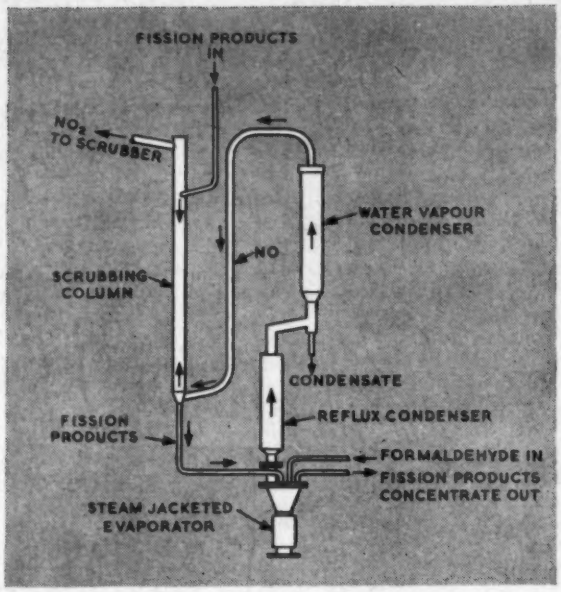


Fig. 1. Continuous evaporation of fission product solutions with formaldehyde destruction of nitric acid.

carbitol and using nitric acid as a salting-out agent, the resulting aqueous solution comprises the highly active waste fission products in addition to a much higher concentration of inert products derived from the impurities of the uranium fuel and from corrosion of the dissolver vessel.

French TBP Process

This is very similar to the above process in that the jacket is removed mechanically or by solution in caustic soda (for aluminium) or 0.5N HNO_3 (for magnesium). After dissolution in strong nitric acid, the uranium metal together with plutonium is extracted by tributyl phosphate, leaving the highly active waste fission products in aqueous solution.

Effect of Composition of Waste on its Subsequent Treatment

From the point of view of concentration, there is a great difference between a nitric acid solution of fission products and one containing a dissolved salt such as aluminium. In the latter case, if the inert salt content is high, as is usually the case, the solution may only be concentrated by a factor of two or three without precipitation occurring, and by a factor of five to ten when taken to dryness. Concentration of nitric-acid solutions of fission products is satisfactorily carried out by distillation. This has to be done at a reduced pressure of 50 to 250 mm Hg, under which conditions ruthenium will not form the volatile tetroxide. The concentration factors attainable with these acid solutions depend primarily on the corrosion and other inactive impurities present, in particular, iron and aluminium. Usually a bulk reduction factor of 50 to 100 is attainable in high acid solutions, 200 to 400 in low acid solutions and 1000 in the dry solid state. Thus, processes using nitric acid as a salting-out agent may require considerably smaller storage space than processes using solid electrolytes as salting-out agents.

As has been pointed out by Glueckauf,[3] the problems of long-term storage and disposal can be considerably eased by removal of the long-lived isotopes Cs^{137} and Sr^{90}, which together represent >99.9% of the toxicity of the 20-year-old fission product solution. Where such removal is possible, the long-term storage problem, in terms of volume, is reduced by factors of the order of 10^4, while the bulk of the fission products, though still requiring short-term storage, may eventually be dealt with by "dispersal".

There is little difficulty in removing, from concentrated fission product solutions, either Sr or Cs. Sr can be precipitated, together with Ba as nitrate by adding concentrated nitric acid, or as sulphate by addition of sulphate ion; and Cs can be precipitated by a number of reagents such as hetero-poly acids, tetra-phenyl boron, and ferrocyanides. Quantitative precipitation becomes more difficult: (a) if the solutions are less concentrated in Sr or Cs; or (b) if the concentration of polyvalent ions is high. In the latter case the activity of the precipitating anions is greatly lowered by the presence of trivalent cations, and a large excess of the precipitating reagent is required. Even then, precipitation is rarely quantitative, and several precipitations with addition of inactive carrier Sr and Cs are necessary. When the aluminium concentration is high, it is not possible to precipitate Sr as nitrate without bringing down large quantities of the fairly insoluble Al $(NO_3)_3$ and as these occlude other fission products as impurity, separations are most unsatisfactory.

Treatment of Waste from Natural Uranium Research

We shall confine the more detailed examination to such solutions which are capable of a high degree of concentration. Discussion of waste from enriched and alloyed fuel elements, the solutions of which would naturally have a high content of inert electrolyte, as well as these processes which use $Al(NO_3)_3$ or NH_4NO_3 as salting-out agents is therefore omitted, and our attention is confined to the products of natural uranium reactors treated with extraction processes in which HNO_3 is used as a salting-out agent. To these belong the British dibutyl carbitol process, the French TBP process and the American Purex process.

Composition of Waste Solutions

Table 1 gives the main constituents and their order of concentration of the type of solution under discussion.

TABLE 1.—Fission Product Highly Active Waste Stream

Concentration Range in grammes metal per litre	
0.2 —1	g, U
0.05 —0.5	g, Fe
0.01 —0.1	g, Cr
0.005—0.05	g, Ni
0.02 —0.2	g, Al
0.01 —0.1	g, Fission products
2.00 —5	Normal HNO_3

Cæsium and strontium form 12% and 6% respectively of the fission products. The main impurities, such as iron, chromium, nickel and aluminium, come from corrosion of the containers, impurities in the uranium metal or inefficient decanning procedures. Fission product content varies with the burn-up in the reactor.

Preliminary Concentration

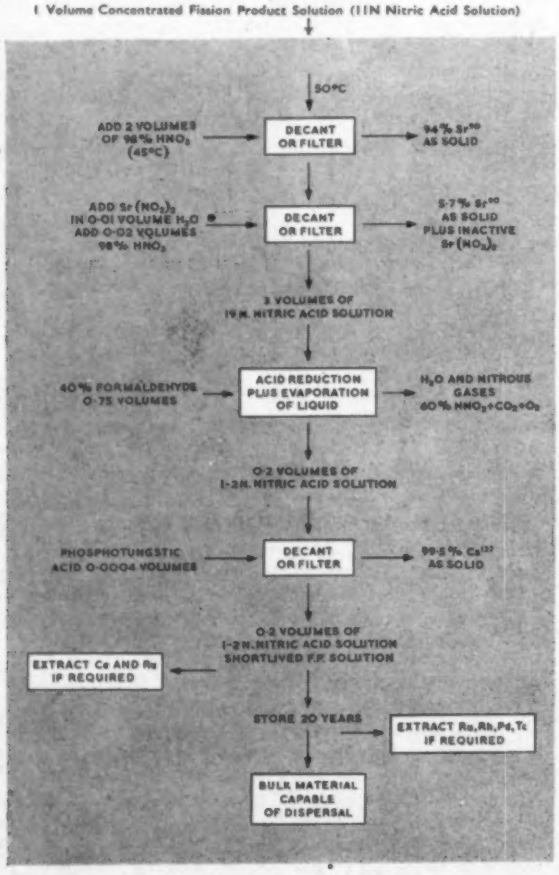
Any practical scheme for the storage of highly-active acid solutions or for separation of fission products should begin with a volume reduction. Direct evaporation *in vacuo* also increases the acidity of the residue (8-12 Normal) and, in order to avoid precipitation of salts, water is added and the solution re-evaporated to a final concentrate at about 2N nitric acid solution with a bulk reduction factor up to 300. An alternative scheme is by the

addition of formaldehyde during evaporation. Formaldehyde reacts with nitric acid to produce nitric oxide at low acidities and nitrogen peroxide at higher acidities.[3] Fig. 1 shows an apparatus for continuous evaporation of fission-product solutions by the addition of formaldehyde to the low-acid solution, the resulting nitric-oxide reacting with partly concentrated fission product solution at high acidity. This method was designed to fit into the disposal scheme outlined in Table 2 below.

Removal of Cs and Sr Together

For the first case, three methods are given[4, 5]: (a) precipitation as the hydroxide of all fission products except the alkali and alkaline earths, (1) by direct ammonia addition, (2) by passage through an anion exchange resin and (3) by electrolytic precipitation through an anion exchanger membrane; (b) solvent extraction, by thiophenoyl trifluoro acetone in a ketone or ether at pH 2-4, of the rare earths and actinides leaving Sr^{90} and Cs^{137} in solution; and (c) taking the fission-product solution to dryness, calcining at 300°C and leaching Cs and Sr nitrates from the remaining insoluble oxides by water. All these methods give good separation of cæsium (90-98%) and rather poorer separation of strontium (60-80%) and they all require prior acid removal. In a disposal treatment it is essential that a decontamination factor of 100 or greater is achieved for strontium-90, as this isotope is the most toxic fission product; thus none of the above methods could be used for this purpose.

TABLE 2—Outline Scheme for Removal of Cs^{137} and Sr^{90} from 50 to 100 fold Concentrated Waste


1 Volume Concentrated Fission Product Solution (11N Nitric Acid Solution)
50°C
ADD 2 VOLUMES OF 98% HNO3 (45°C)
DECANT OR FILTER
94% Sr90 AS SOLID
ADD Sr(NO3)2 IN 0·01 VOLUME H2O ADD 0·02 VOLUMES 98% HNO3
DECANT OR FILTER
5·7% Sr90 AS SOLID PLUS INACTIVE Sr(NO3)2
3 VOLUMES OF 19 M. NITRIC ACID SOLUTION
40% FORMALDEHYDE 0·75 VOLUMES
ACID REDUCTION PLUS EVAPORATION OF LIQUID
H2O AND NITROUS GASES 60% HNO3+CO2+O2
0·2 VOLUMES OF 1·2 M. NITRIC ACID SOLUTION
PHOSPHOTUNGSTIC ACID 0·0004 VOLUMES
DECANT OR FILTER
99·5% Cs137 AS SOLID
0·2 VOLUMES OF 1·2 M. NITRIC ACID SOLUTION SHORTLIVED F.P. SOLUTION
EXTRACT Ce AND Ru IF REQUIRED
STORE 20 YEARS
EXTRACT Ru, Rh, Pd, Tc IF REQUIRED
BULK MATERIAL CAPABLE OF DISPERSAL

Individual Removal of Strontium

The insoluble salts of strontium—the sulphate, carbonate and phosphate—cannot be considered for direct precipitation from fission product solutions. From NHO_3 solutions they either do not precipitate strontium quantitatively in the presence of three-valent ions or else they also precipitate many of the impurities and other fission products (see Table 1). The most suitable method appears to be removal in the form of nitrate from strong acid solutions and this also has the advantage of avoiding the addition of solid chemicals which is always a disadvantage in a disposal scheme. Strontium nitrate is practically insoluble in 18-19N nitric acid solution, and on precipitation from fission-product solutions it is usually contaminated by barium, lead and a little cerium[144]. It can be made >99% radiochemically pure by a second precipitation from nitric acid. In the presence of a high concentration of aluminium, precipitation of strontium from strong nitric acid occurs together with much of the aluminium. This in turn brings down some 20% of the activity occluded on the aluminium. However, by carrying out the precipitation at higher temperatures (50-60°C) the aluminium does not precipitate with the strontium and consequently the latter is much less contaminated with extraneous activity. The solubility of strontium in nitric acid also increases with temperature, but much less than that of aluminium. In a disposal scheme the increased amount of Sr^{90} in the mother liquor is a grave disadvantage, so a second precipitation is carried out with addition of inactive carrier. Lead, barium and strontium nitrates are suitable for this purpose and their scavenging efficiency increases in that order.

Direct Removal of Cæsium

Several methods are possible for the direct precipitation of cæsium from fission product solutions; they are briefly reviewed below.

Cæsium Alum

This salt has a lower solubility than the lighter alkali alums. The separation process requires first the neutralisation of the fission product waste with alkali to *p*H 2 to 4.5, then the addition of potash alum to the hot solution from which the latter salt precipitates, carrying over 95% of the cæsium. Repetition of this procedure produces a highly concentrated cæsium alum. This process suggested by Gresky[6] is not satisfactory for the low salt content HNO_3 solutions under discussion, but is much more useful for extracting cæsium from alkaline wastes.

Tetraphenyl Boron Cæsium

This salt is very insoluble and 99% of cæsium can be removed from concentrated fission product solution by the addition of tetraphenyl boron sodium solution. As there are settling and filtering difficulties associated with this salt, the precipitation should be carried out in 0.2 to 0.7N nitric acid solution in the cold and the mother liquor should be separated within an hour. On heating the separated boron salt with sulphuric acid up to 600°C, cæsium sulphate is obtained. As a possible industrial process, this method suffers from three disadvantages: (a) the rigorous precipitation conditions; (b) the expense of the reagent; and (c) the general desire of atomic-energy plants tc avoid the use of boron compounds.

Metal Ferrocyanide Method

This method was suggested by American workers[7] for the removal of cæsium from fission-product solutions saturated or nearly saturated in aluminium. The separation procedure works most efficiently in solutions of high *p*H (6-10). Our work with HNO_3 solutions of fission products shows[8] that addition of slight excess of alkali

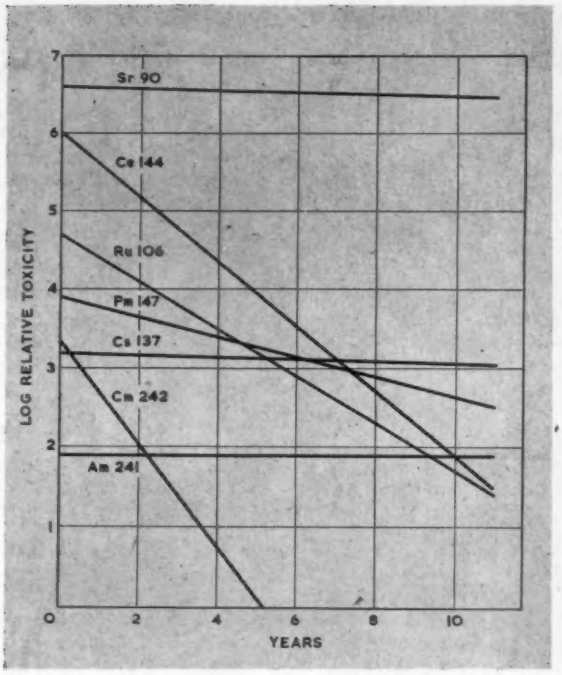


Fig. 2. Relative toxicities of waste solutions from processing irradiated natural uranium.

Fig. 3. Changing stainless-steel valves by remote control manipulators at Harwell

ferrocyanide precipitates cæsium in good yield (>80%) if the acidity is below one normal nitric acid. The precipitate on treatment with ammonia releases cæsium quantitatively to solution, at the same time separating it from impurities. This process can be used industrially but the problem of cyanide decomposition by irradiation has to be watched.

Cæsium Precipitation as the Phosphotungstate

Cæsium can be precipitated quantitatively from concentrated-fission-product solutions as the dicæsium hydrogen phosphotungstate.[9] This separation can be carried out in nitric acid solution of concentrations from 0.5 to 16N nitric acid solution giving a heavy precipitate with good settling properties. This salt has the advantages of being precipitated with very little impurity except rubidium, and the conditions of precipitation are most suitable for nitric-acid fission-product solutions. Cæsium can easily be separated from the phosphotungstate group after dissolution in ammonia, either by addition of baryta or by ion-exchange procedures.

Further Fission Product Extractions after Removal of Sr and Cs

Extraction of Ce and Ru

Ce-144 and Ru-106 can be extracted for use as radiation sources if required; if removed from one-year-old fission products, their curie level activities relative to that of cæsium would be 25 and 2 times respectively, making a large amount of radiation available.

The addition of sodium bromate to concentrated fission-product solutions 2N in nitric acid followed by extraction with 50% tributyl phosphate in an inert diluent removes practically all of the cerium as the tetravalent nitrate (the partition coefficient, K, is about ten) and no ruthenium is extracted. Alternatively, the cerium can be precipitated as the iodate. By using a more powerful oxidising agent, sodium bismuthate, extraction with 50% TBP in carbon tetrachloride takes up both the oxidised cerium (with a distribution factor $K \simeq 40$) and the ruthenium ($K \simeq 50$). Both are completely recovered from the organic phase by washing with H_2O_2 solution. Ruthenium alone can be removed from concentrated fission-product solutions 2N in nitric acid by the addition of an oxidising agent such as bromate, bismuthate or permanganate and boiling off the ruthenium tetroxide.

Extraction of Valuable Rare Metals from 20-Year-Old Solutions

While it would not be economical to recover from the highly active solutions the rare and practically inactive metals Ru, Rh and Pd, such a process becomes feasible for solutions of more than 15 years of age, after the long-lived Cs and Sr have been previously removed (see Ref. 3). These rare metals could be extracted by several methods, such as sulphide precipitation or by electrolysis. The rhodium would be completely inactive but the palladium would contain 20% of Pd^{107} of 5×10^6 years half-life, and the inactive ruthenium would be contaminated with a few millicuries of RU^{106}. Technetium-99 (half-life 2×10^5 years), useful because of its anti-corrosion properties, could also be isolated along with the group 8 metals.

Integration of Cs and Sr Removal in a Disposal Scheme

Prior to any process for removal of these elements from a fission-product-waste solution, such as given in Table 1, a concentration step would be necessary. This could best be carried out by direct distillation at atmospheric pressure or preferably under vacuum. The degree of concentration without causing precipitation of solids depends on the alkaline earth, iron and particularly aluminium content, and is usually of the order of 50 to 100. Increase of the acidity of this solution up to 19N nitric acid solution by addition of 98% nitric acid and leaving overnight at 50°C causes the precipitation of, say, 94% of the Sr^{90} content. The addition of a similar quantity of

inactive strontium for a second precipitation increases this figure to 99.7%. The material resulting from the first precipitation can be kept either for use as radiation sources or for separate disposal, and that from the second precipitation for disposal only. The next step consists of a deacidification-cum-evaporation step using CH_2O, and this provides a further reduction in volume at an acidity of 1-2N nitric acid solution. Threefold excess of phosphotungstic-acid precipitates >99% of the cæsium, leaving a 1-2N nitric acid solution of short-lived fission products which can either be worked up for further radioactive materials or stored for 10-20 years prior to "dispersal". A general block flowsheet is shown in Table 2.

LIMITATIONS OF DISPOSAL SCHEME

This process combines the separation of the two long-lived isotopes which comprise the greatest hazard and the most valuable radiation sources into small bulk to be "contained" or purified for use. The remaining short-lived material in large bulk should be "dispersible" after 20 years. If this process is worked on a sufficiently large scale, it may not be possible to "disperse" this short-lived material, as there would then be present comparatively large quantities of long-lived rare earths (Sm^{151} and Pm^{147}) to make such "dispersal" hazardous. This material would then have to be stored for much longer periods and it may be more economic to "fix" this activity as a ceramic. In future reactors when high burn-up of natural or enriched uranium or plutonium occurs, americium-241 is produced in quantity, e.g., from the action of neutrons on U^{238}. This actinide remains with the fission-product waste stream and hence the toxicity of 20-year-old waste after removal of strontium and cæsium is then governed by the quantity of Am^{241} present. Fig. 2 shows that in the case of natural U irradiated at a flux of 10^{13} n/cm²/sec. and a load of 1500 MW day per tonne of uranium, the contributions of Cm and Am to the toxicity of the fission products are negligible.

Handling of Highly Active Materials

Owing to the well-known highly toxic nature of most medium and long-lived radioisotopes, both as radiation and ingestion hazards, it is essential for the health and safety of personnel to have thick shielding around the plant, plus an excellent ventilation system together with ancillary health physics monitoring staff. The expensive biological shield, usually made of barytes concrete several feet thick, surrounds a stainless-steel plant which has to be operated remotely.

Four types of separation processes are discussed:

(a) Solvent extraction where one constituent is extracted from an aqueous solution. This is the simplest system to work remotely, as gravity feeds are used and no valves are required. This continuous process is used in most reactor fuel processing, but because of low-solvent-extraction rates is of little use for separating fission products, particularly alkalis and alkaline earths;

(b) Classical precipitation methods are used for batch processing. Removal of mother liquor can be troublesome if precipitates do not settle well and a large "heel" of liquor is sometimes unavoidable. This method would be more satisfactory if centrifugation were used and the development of a continuous centrifuge would be even more desirable;

(c) Distillation is not practicable for fission-product separation from solution, but may prove to be attractive in the future in connection with high-temperature processing of reactor fuels; and

(d) Ion-exchange separation procedures can be used particularly for purification of individual fission products. Organic exchangers are limited by radiation breakdown of the material, but inorganic exchangers, for example, zirconium phosphate, are more stable to radiation and may be utilised in the future.

In a stainless-steel plant all movements of liquids must be known, for example, by having pneumercators in the system. Highly active liquids should always be moved by suction or gravity and not by positive pressure. Preferably there should be no valves, taps or filters in the system; if they are present it should be possible to service them by remote control. Solids produced during the separation or purification processes should always be dissolvable in order to remove them. If attempts are made to remove highly active solids as slurries and a blockage occurs, then a whole section of the plant may become unusable.

For purification procedures it is often desirable to see part of the process. This can be done by incorporating in the cell a cerium glass plus a window of zinc-bromide solution. Apparatus can then be worked from outside by using master-slave manipulators. Fig. 3 shows one such viewing cell at Harwell. Metal valves and filters can be removed and replaced if necessary from this stainless-steel pilot plant by the manipulators. It is also essential to have analytical control at many points on fission-product separation processes. This requires sampling equipment, often very elaborate, together with a shielded ancillary facility for sample dilution and chemical or radiochemical analysis.

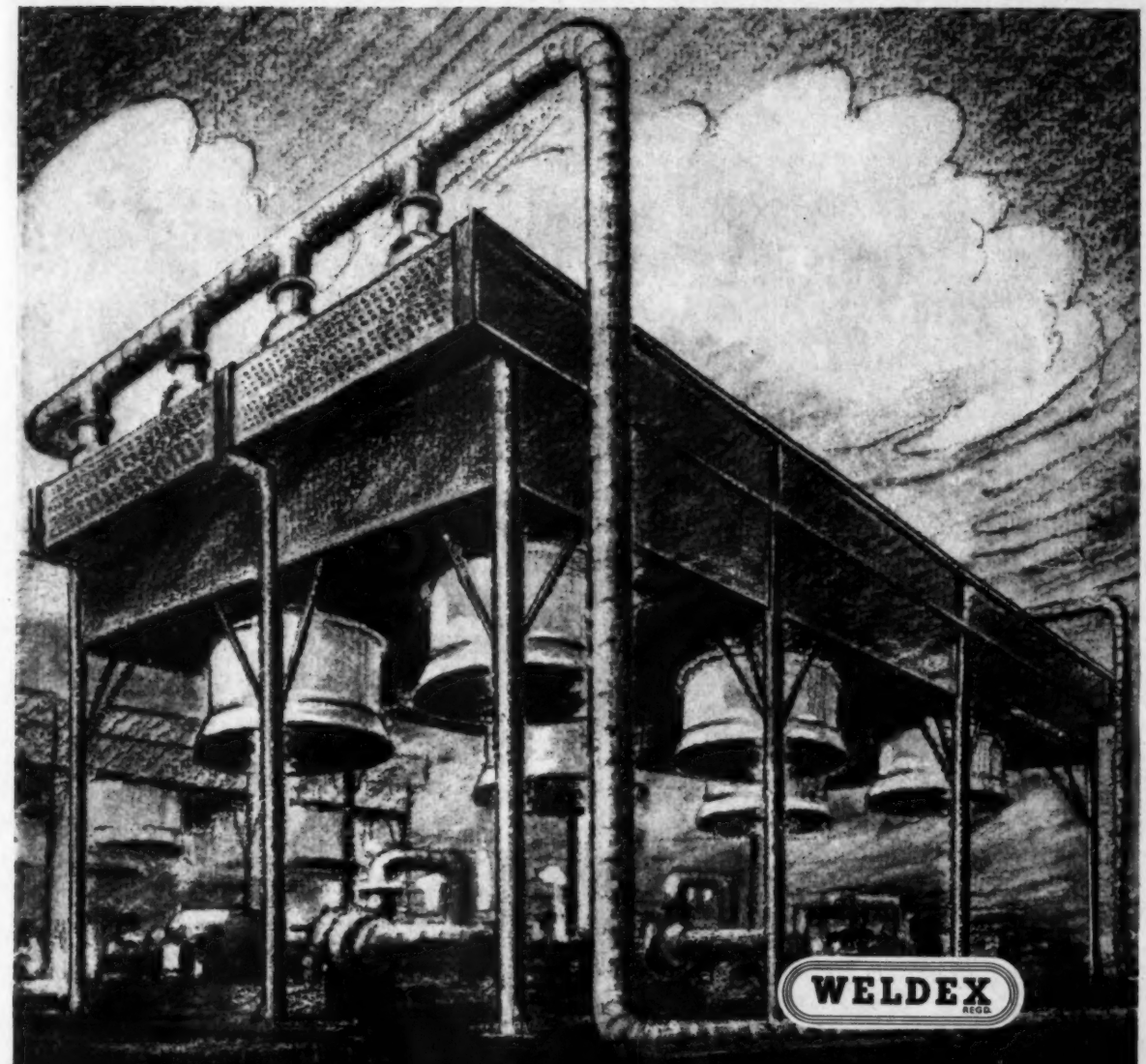
REFERENCES

[1] Geneva Conference on Peaceful Uses of Atomic Energy, Vol. 9, Paper 398, U.N.O., 1955.
[2] Glueckauf, E. *Chem. and Proc. Eng.*, 1956, **1**, 23.
[3] Healy, T. V. *J. App. Chem.* In the Press.
[4] Healy, T. V., Carter, P. E., and Brown, P. E. Progress in Nuclear Energy, Vol. 3, Paper 34. Pergamon Press Ltd., 1956.
[5] Healy, T. V., and Glueckauf, E. Geneva Conference on Peaceful Uses of Atomic Energy, Vol. 9, Paper 415, U.N.O., 1955.
[6] Gresky, A. T. Oak Ridge National Laboratory Report No. 742, Atomic Energy Commission Report No 2999 (1951).
[7] Burgess, W. H., and Miller, H. W. Nuclear Engineering and Science Congress, Cleveland, 1955, Paper 225.
[8] Burns, R. E., and Stedwell, M. J. Nuclear Engineering and Science Congress, Philadelphia, 1957, Paper 58.
[9] Healy, T. V. *J. Inorg. and Nuc. Chem.* In the Press.

Radiation Sources for Chemical Processes

An historic stage in development was represented by the decision of the International Atomic Energy Agency to call a conference on the application of large radiation sources in industry. This recent gathering in Warsaw was convened to discuss especially the application of such sources to industrial chemical processes. More than 40 papers from 11 countries had been notified ahead of the opening date, covering equipment (including measuring instruments), fundamental studies of chemical kinetics, applied investigations and the germ of ideas about production. The British contribution of six papers included one devoted solely to studies of chemical production using fission fragments. In many countries considerable attention has evidently been paid to the field of polymerisation—modifying the properties of polymers by ionising radiation, production of polymers, of grafts and co-polymers. Perhaps it is a bit early to expect realistic cost-studies, but only two papers were explicitly devoted to this subject. Incidentally, a survey earlier in the year in *Khimicheskaya Promyshlennost*, 1959, No. 2, p. 99, by M. A. Proskurnin did discuss this among other industrial aspects for a number of reactions. Success in these lines of work would happily convert the sources of an embarrassing disposal problem into new productive assets.

BCE 6134 for further information



Air-Cooled HEAT EXCHANGERS

Heat Exchange Division
WELLINGTON TUBE WORKS LTD

MASS TRANSFER ON BUBBLE-CAP AND SIEVE PLATES*

THE total resistance to the flow of gas on a bubble-cap or sieve plate is the sum of three indvidual resistances[1] as follows:

$$\triangle p_t = \triangle p_d + \triangle p_\sigma + \triangle p_{st} \quad \ldots . (1)$$

where $\triangle p_t$ = total resistance of plate and liquid;
$\triangle p_d$ = resistance of dry plate;
$\triangle p_\sigma$ = resistance due to surface tension; and
$\triangle p_{st}$ = resistance of static liquid layer on plate.

It is clear that the resistance of the liquid to the gas flow, $\triangle p_l$, is the sum of the individual resistances $\triangle p_\sigma + \triangle p_{st}$, and constitutes the total amount of energy consumed in the creation of the surface of contact between the gas and the liquid, and in mass transfer. It is natural to suppose, therefore, that this loss of energy must be directly connected with the mass-transfer process. For this reason, data on mass transfer in the gas phase on bubble-cap and sieve plates were correlated by means of a relation of the form:

$$\frac{\triangle p_l}{K_{og}a} = f(G_k) \quad \ldots . (2)$$

where $\triangle p_l$ = liquid resistance to gas flow;
$K_{og}a$ = mass-transfer coefficient, based on unit area of plate surface (on which the bubble-caps are arranged, or the perforated area of a sieve plate); and
G_k = velocity in the free cross-section of the column.

Data from about 700 experiments were correlated in this way; the experiments were carried out on the absorption of ammonia in water on bubble-cap and sieve plates, and for a wide range of values of the flow-rates and plate dimensions. The conditions were such that the diffusional resistance of the liquid phase was reduced to a minimum. Since the extent of this resistance remained unknown, however, the results were correlated in terms of the overall coefficient $K_{og}a$, and not the gas-phase coefficient K_ga.

The resulting correlations are plotted in Figs. 1 and 2† for sieve plates and bubble-cap plates respectively, and it is seen that the experimental points, each of which corresponds to 2 to 9 experiments for the same flow-rates and plate dimensions, are grouped closely around curves which are of the same character for both types of plate. The only exceptions were the points for sieve plates with an orifice diameter $d_o = 0.9$ mm, and for bubble-cap plates where the height of the outlet weir $h_w = 7$ mm, i.e., where the height of liquid above the slots was equal to zero. These points were not included in the correlation.

The fact that, in spite of the variation over a wide range of the plate dimensions (orifice diameter, slot dimensions, height of the outlet weir, free cross-section, cap diameter) and of the flow-rates (liquid wetting rate), all the points fall around single curves for the two types of plate, shows that the mass transfer is determined by two main factors: the gas velocity in the free cross-section of the column, G_k, and the liquid resistance to the gas flow, $\triangle p_l$.

Replotting the data given by the authors in their Figs. 1 and 2 on a logarithmic basis gives two straight lines (see Fig. 3 in authors' original paper), the equations for which are as follows:

Bubble-cap plates

$$K_{og}a/\triangle p_l = 355\ G_k^{1.32} \quad \ldots . (3)$$

Sieve plates

$$K_{og}a/\triangle p_l = 240\ G_k^{0.76} \quad \ldots . (4)$$

It follows from Fig. 3 that for $G_k < 0.5$ m./sec., the mass-transfer coefficients for sieve plates are greater than those for bubble-cap plates. For $G_k > 0.5$ m./sec., mass-transfer coefficients are greater for bubble-cap plates.

In using Equations (3) and (4) in design, it is only necessary to know the resistance of the plate and liquid, and that of the dry plate, since:

$$\triangle p_l = \triangle p_t - \triangle p_d \quad \ldots . (5)$$

Equations are available in the literature from which $\triangle p_t$ and $\triangle p_d$ can be calculated.

Equations (3) and (4) can be rearranged so as to give the number of transfer units, as follows:

Bubble-cap plates

$$N_{og} = 0.0986\ G_k^{0.32}\ \triangle p_l(A_T/A_K) \quad \ldots . (6)$$

Sieve plates

$$N_{og} = 0.067\ G_k^{-0.24}\ \triangle p_l(A_T/A_K) \quad \ldots . (7)$$

where N_{og} = number of transfer units for system ammonia/water;
G_k = velocity in free cross-section of column (m./sec.);
$\triangle p_l$ = liquid resistance to gas flow (mm water); and
A_T/A_K = ratio of area of perforated part of plate (for sieve plates), or area of plate on which bubble-caps are arranged (for bubble-cap plates), to column cross-section.

For gas/liquid systems other than ammonia/water, an estimate of the value of the gas-phase mass-transfer coefficient can be made by means of the method proposed by GERSTER and CALDERBANK[2]:

$$(N_{g_1}/N_{g_2}) = (\mathrm{Pr}_1/\mathrm{Pr}_2)^{\frac{1}{3}} \quad \ldots . (8)$$

where the suffix 1 refers to the ammonia/water system and the suffix 2 to any other gas/liquid system (Pr = Prandtl number).

REFERENCES

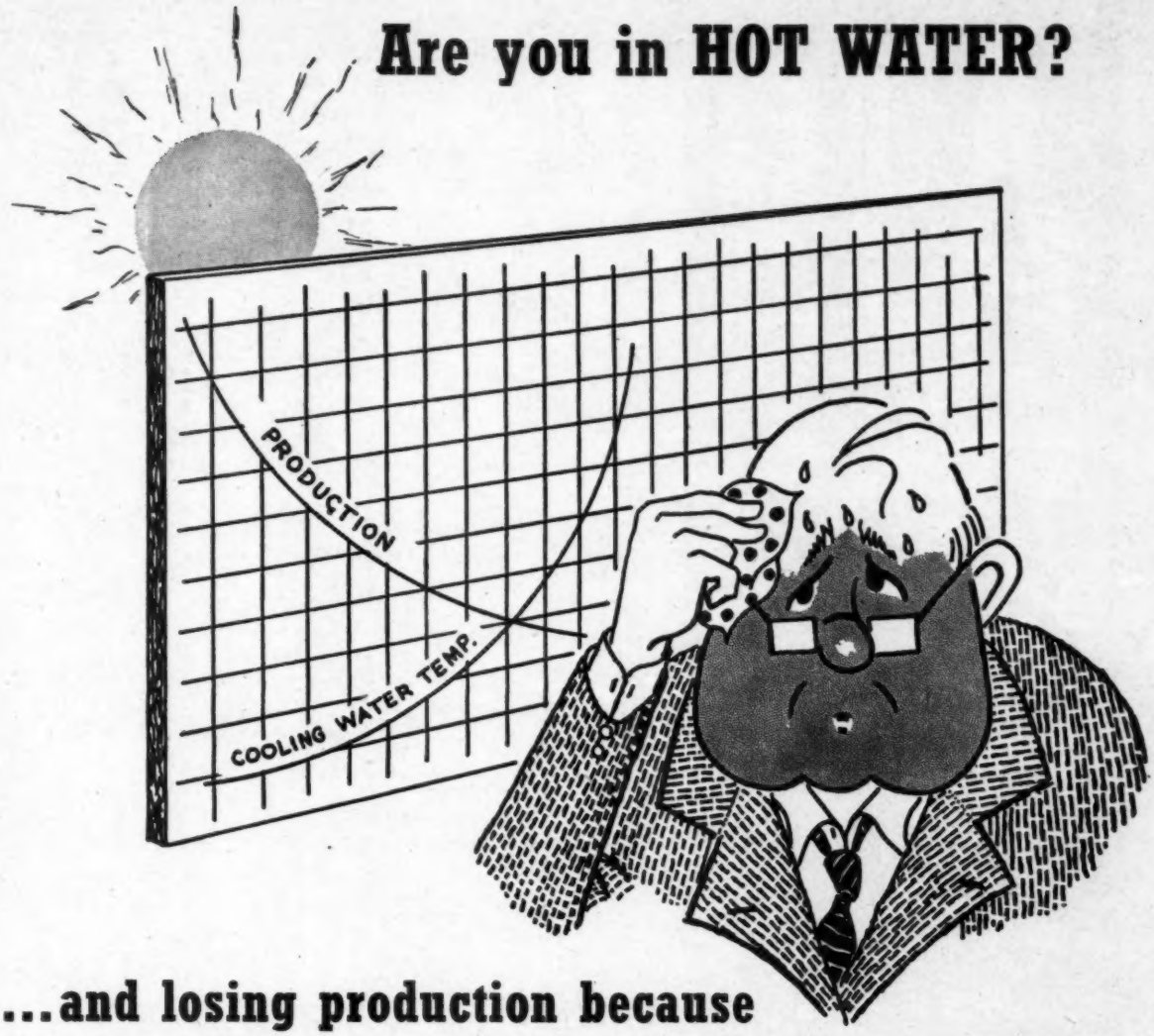
[1] Usyukin, I. P., Aksel'rod, L. S. *Kislorod*, 1949, No. 1, 5; Aksel'rod, L. S., Trudy *Vniikimash*, 1956, No. 1, 22; Aver'yanov, I. G. Thesis MIKhM, 1956.

[2] Gerster, J. A., Bonnet, W. E., Hess. *J. Chem. Eng. Prog.*, 1951, **47**, No. 10, 523; 1951, **47**, No. 12, 621; Calderbank, P. H. *Trans. Inst. Chem. Eng.*, 1956, **34**, No. 1, 79.

* Translated by J. Jackson from the original article by A. N. Planovski, V. I. Matrosav, O. S. Chekov and G. P. Solomaka which appeared in *Khim. Tech. Top. Mas.*, 1958, No. 3, 30.

† Figs. 1, 2 and 3 are given in the authors' original paper.

Are you in HOT WATER?



...and losing production because your cooling water temperature is too high

Head Wrightson Processes offer the well known high efficiency Fluor Cooling Tower with guaranteed cold water temperatures. We design, manufacture and erect prefabricated timber and precast concrete induced draught cooling towers for all purposes.

Consult us now and ensure that your production does not suffer in the future

We invite you to write for details of this equipment

HEAD WRIGHTSON PROCESSES LTD

TEESDALE HOUSE 16/26 BALTIC STREET LONDON EC1

Offices at: P.O. Box 1595 **SYDNEY** P.O. Box 1034 **JOHANNESBURG** P.O. Box 2608 **CALCUTTA** and P.O. Box 706 **HAMBURG**

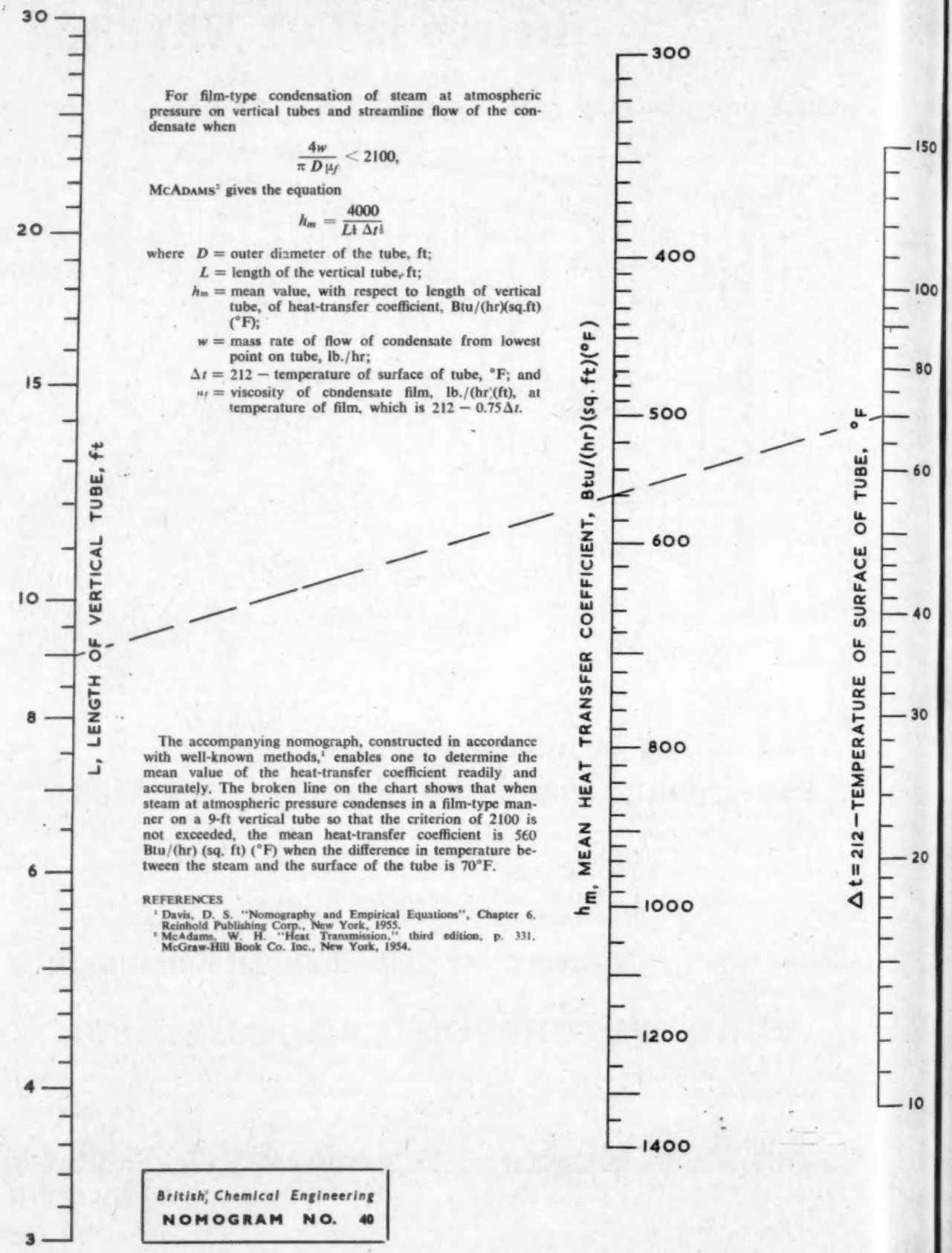
Associates in the U.S.A.: The Flour Products Company · Los Angeles 22 · New York · Chicago · Tulsa, etc.

P 179

HEAT-TRANSFER COEFFICIENTS FOR STEAM CONDENSING ON VERTICAL TUBES

by D. S. DAVIS

Head, Department of Pulp and Paper Technology, University of Alabama



For film-type condensation of steam at atmospheric pressure on vertical tubes and streamline flow of the condensate when

$$\frac{4w}{\pi D \mu_f} < 2100,$$

McAdams[2] gives the equation

$$h_m = \frac{4000}{L^{\frac{1}{4}} \Delta t^{\frac{1}{3}}}$$

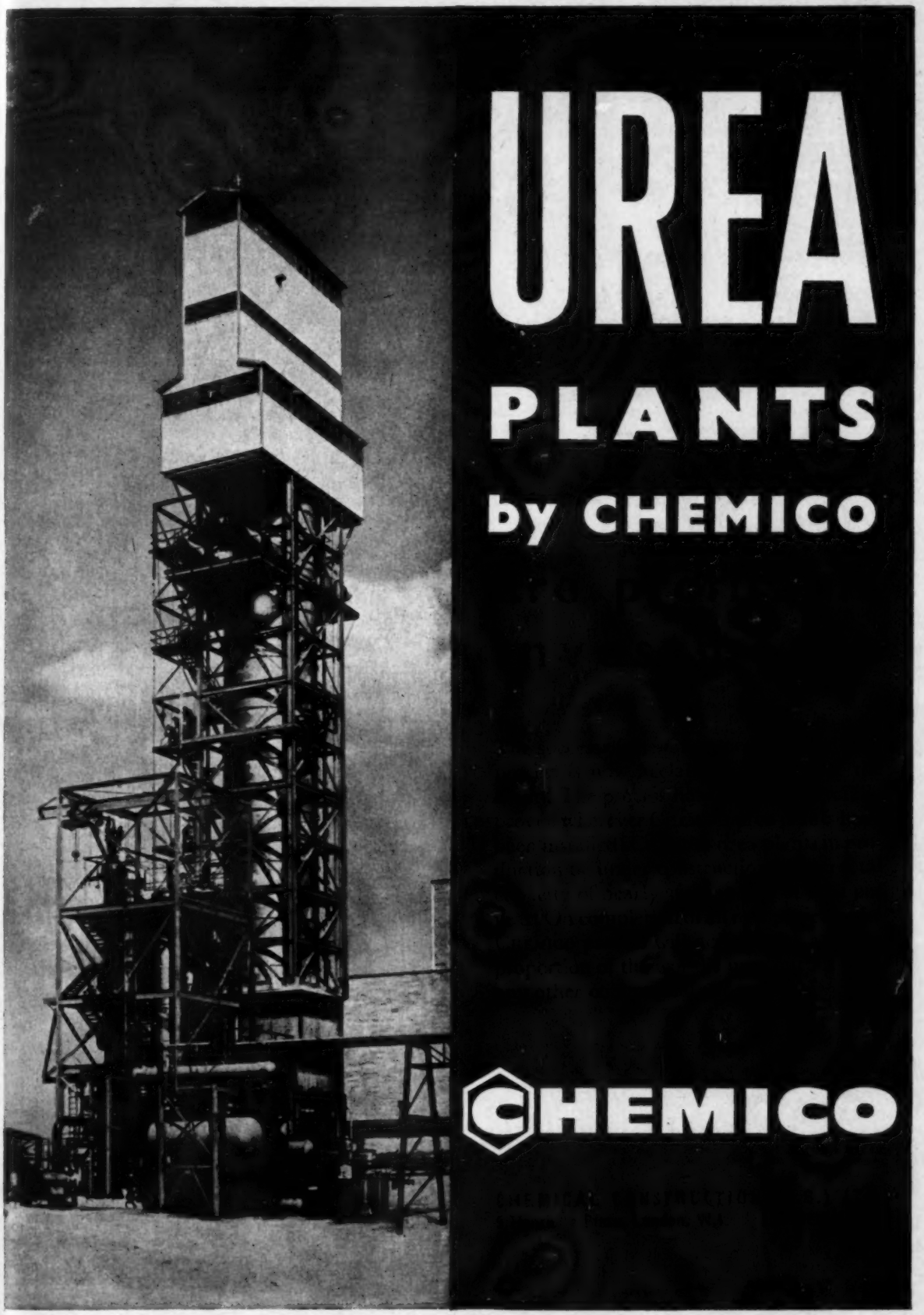
where D = outer diameter of the tube, ft;
L = length of the vertical tube, ft;
h_m = mean value, with respect to length of vertical tube, of heat-transfer coefficient, Btu/(hr)(sq.ft)(°F);
w = mass rate of flow of condensate from lowest point on tube, lb./hr;
Δt = 212 − temperature of surface of tube, °F; and
μ_f = viscosity of condensate film, lb./(hr)(ft), at temperature of film, which is $212 - 0.75\Delta t$.

The accompanying nomograph, constructed in accordance with well-known methods,[1] enables one to determine the mean value of the heat-transfer coefficient readily and accurately. The broken line on the chart shows that when steam at atmospheric pressure condenses in a film-type manner on a 9-ft vertical tube so that the criterion of 2100 is not exceeded, the mean heat-transfer coefficient is 560 Btu/(hr) (sq. ft) (°F) when the difference in temperature between the steam and the surface of the tube is 70°F.

REFERENCES

[1] Davis, D. S. "Nomography and Empirical Equations", Chapter 6. Reinhold Publishing Corp., New York, 1955.
[2] McAdams, W. H. "Heat Transmission," third edition, p. 331. McGraw-Hill Book Co. Inc., New York, 1954.

British Chemical Engineering
NOMOGRAM NO. 40

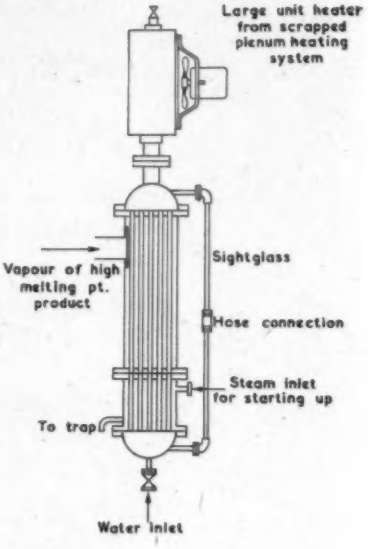

UREA
PLANTS
by CHEMICO
CHEMICO

PROCESS ENGINEER'S NOTEBOOK

Unit Heater Used as an Air-cooled Condenser

A SMALL PILOT-PLANT condensation system similar to that described in an early issue of this journal (*B.C.E.*, 1, 2, 1956) was required for a high-boiling-point chemical. As with the earlier process, the object was the purification of the material by distillation; at the same time solidification of the condensate had to be prevented. Instead of boiling carbon tetrachloride, water was used for removing the latent heat of the condensing substance; another departure was the replacement of the upper water-cooled condenser used in the original scheme for condensing and returning the cooling medium to the main condenser by an improvised air-cooled condenser. This was a convenient arrangement, since it avoided the erection of the water supply pipelines to the upper condenser; further, since the air-cooled condenser was actually a large scrapped unit heater, the expense of the water-cooled condenser was spared.

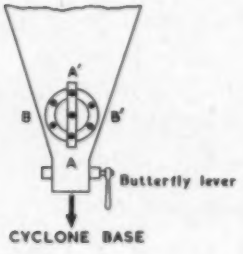
The heater converted consisted of 27 gilled 18 g. tubes, $\frac{1}{4}$ in. o.d. on the plain tube, each just short of 3 ft in length. It was used in the inverted position, that is, with the original steam connection facing downwards and connected to the tube side of the main condenser. A vent valve was fitted at the connection provided normally for the steam trap.

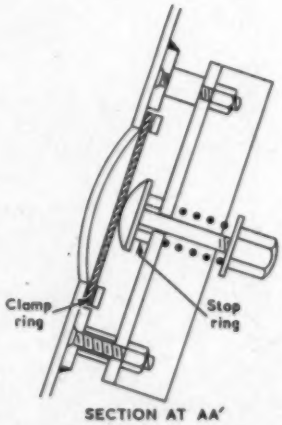


Overcoming Bridging in Small Cyclones

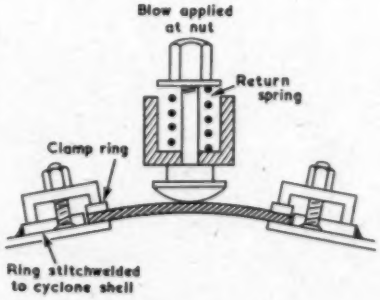
IN A DRY GRINDING PLANT employing air-swept swing-hammer mills the ground product was collected in the usual manner in cyclones. Trouble was frequently experienced with bridging or packing just above the butterfly discharge valve at the base of each cyclone. This interfered with the periodical discharge of the ground product. Even when the somewhat crude butterfly valves were replaced by rotary air locks the trouble still persisted.

The plant operators attempted to overcome this difficulty by hitting the cyclone base with a mallet. As the sheet used in the construction of the cyclones was thin, the latter soon became badly dented at their bases, and in the case where the butterfly discharges were still fitted it became difficult to open and close them. To solve the problem it was decided not to go to the expense of installing vibrators on the cyclones; instead, an opening was cut at a point near the cyclone base. This was covered by a circular piece of sheet rubber attached to the cyclone shell by a ring bolted direct to a reinforcement welded to the shell. Over this was fitted a short length of channel section carrying a spring-loaded plunger which was adjusted so that it rested lightly against the rubber diaphragm. The outer end of the plunger terminated in a blind nut which was occasionally given a sharp blow. This was sufficient to loosen material adhering to the wall of the cyclone, and to permit a ready discharge of product.





SECTION AT AA'



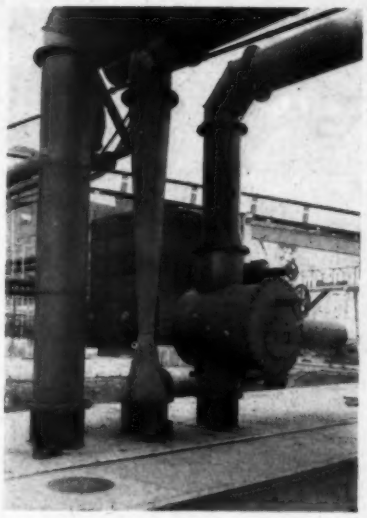
SECTION AT BB'

T.W.

A Venturi Damper for Eliminating Gas Pulsations in Pipelines

NOTED DURING A RECENT VISIT to the Pleck Gas Works, Walsall, was a novel method of reducing the gas pulsations in pipelines which can arise where gas transference is carried out by reciprocating or lobe-type compressors. Pulsations can upset the operation of the equipment being fed by the compressors, such as the gas-washing and purification sections of a plant. They can set up vibrations in the pipework system with the risk of serious damage to the pipework and its supporting structures. The pulsations can be even greater if compressors are operated in parallel. Although their nominal speeds may be the same, it is possible to have just enough difference for a beat effect to be set up. This will lead to intermittent high-frequency vibrations, which are not only likely to produce physical damage to equipment, but are also a nuisance through the noise produced during the period of vibration.

The apparatus in use at the Pleck Works is shown in the accompanying photograph; it is a simple venturi section fitted in the gas pipework. Underlying its application is the assumption that the pulsations are high-velocity movements of the gas; the purpose of the venturi is to give the gas at the throat a velocity equal to or approaching closely the velocity of the gases corresponding to the pressure fluctuations; in the diffuser the gases expand and emerge substantially free from pressure fluctuations. Ideally, the entire volume of the gases should reach the velocity of sound at the throat, but as this is not practical, a lower velocity, say 50% of the sonic velocity, is sufficient to reduce adequately the magnitude of the fluctuations. The high proportion of the kinetic energy generated at the throat converted to pressure energy at the end of the diffuser is an important advantage of this type of damper. For this reason, the device wastes very little power.



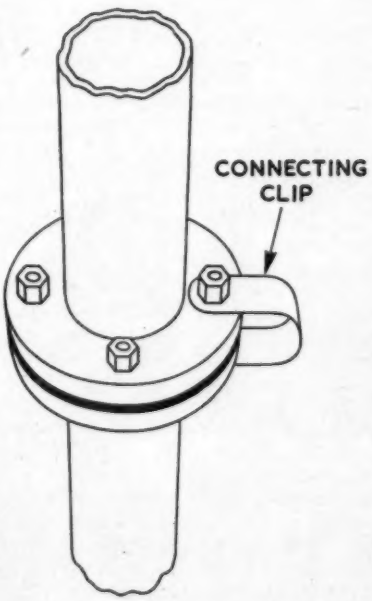
The accompanying photograph also shows an earlier type of damper. The box contains a fixed perforated screen that can be by-passed by means of a branch connection. The amount of by-pass gases is governed by means of a valve. The vibrations can be tuned from the gas stream by adjusting both the by-pass valve and the relative positions of the two screens. The back-pressure set up is not serious but a disadvantage of this damper is that it has to be set for each value of the gas flow. Of these two dampers, not only is the venturi arrangement the more compact, but it is effective over a wide range of gas flows. The pressure loss is about 1½ in. w.g. and the quantity of gas passing through is six million cu. ft a day at a pressure of 60 in. w.g.

(Courtesy of W. C. Holmes Ltd., Huddersfield)

Reducing Fire Hazard from Static

A NUMBER OF FLANGED pipework joints, each with a metal loop bolted across the outside faces of the flanges, aroused curiosity during a visit to a plant manufacturing nitrile rubber. The reason for these strips is to prevent the risk of an accumulation of static electricity during the transference of the processing liquids through the pipes, in this case butadiene and acrylonitrile. The inflammable nature of both these liquids emphasises the extent of the hazard. The strips shown (see the accompanying diagram) were used rather than rely upon the contact between bolt head and nut at the outer flange faces which would have a high electrical resistance.

Among other safety measures observed at this plant were the enclosure of the gland and gear drive coupling of the agitator shaft of the polymerisation vessels. For this purpose close-fitting sheets of transparent plastic material were attached to the supporting structure of the motor-gear unit. Another safety measure was to fit line-blank valves above the lubricated plug valves in the reactant transfer lines to the polymerising vessels. During maintenance operations carried out inside a polymeriser there would, therefore, be no risk of toxic materials entering the vessel.



Acknowledgment: THE DISTILLERS CO. LTD.

Contributions invited

THE EDITOR invites readers to submit, for possible publication in "Process Engineer's Notebook", notes on practical devices that have been elaborated on the job for improving the operation or increasing the safety of processes, or that have been extemporised in special circumstances. The contributions preferably should be of about 250-500 words, and be illustrated with a line diagram or sketch, or a photograph. A minimum of three guineas will be paid for each contribution used. They will be published anonymously or under the contributor's name, according to his wishes.

AMERICAN LETTER

The Cost of Progress

DURING the last three years, the U.S. chemical industry has invested more than 4.5 billion (U.S.) dollars in new capital equipment, and some major companies have increased their fixed assets by an average of 40%. It is unfortunate that a quick return on this huge outlay was held up by the general recession of 1958, which coincided with the completion of many new projects. Consequently, the double effect of heavy spending and a reduced turnover has severely trimmed the profits of many chemical concerns, as well as the earnings of construction companies, equipment manufacturers, consultants and so on.

The Expansion Cycle

As chemical production grows more complex and the installation of large, specialised process units becomes increasingly necessary, the tendency for the industry to expand in a series of jumps is most marked. In numerous cases, the extra capacity made available is well in excess of immediate requirements. Hence, it is difficult to see how periods of reduced earnings can be entirely avoided, particularly when no antidote for irregular consumer demand has yet been found. Indeed, the pattern already seems to be established, since three periods of expansion and consolidation have arisen in the post-war period, namely, 1947 to 1949, 1953 to 1955 and 1957 to 1959. The effect on associated industries such as construction and plant manufacture is considerable. For instance, in 1947, the capital outlay of the chemical industry was $1060 million, which fell to $670 million in 1949, while a new high level of about $1560 million reached in 1953 fell to $1016 million in 1955. In the latest cycle, a record expenditure of $1724 million attained in 1957 is anticipated to sink to about $1288 million in 1959. Nevertheless, the overall expansion in annual outlay from $800 million in 1946 to $1724 million in 1957 is the significant item and a new record of $2000 million may be reached in 1961.

Chemical Production

As regards chemical production, a disquieting feature was the drop in output which commenced in the latter part of 1957 and persisted throughout a large part of 1958. This was unusual for the industry, since the U.S. production of chemicals had grown fairly steadily from 1947 onwards and in a decade had doubled in size. According to Federal Reserve Board figures, taking 1947 to 1949 as an index of 100, a peak of 205 was reached about mid-1957, which fell back to the 1955 figure of 182 in the spring of 1958. So far, the rate of recovery for the chemical industry has not been substantially greater than the 12% recovery rate for industry in general. However, long-term confidence in the chemical industry is good, since the rate of growth has been about two and a half times the rate for all industry. On this basis, the chemical production index should reach 250 when the total industrial production index reaches 160, which may occur in 1961.

This optimism is associated also with the more direct requirements of the consumer goods industries, such as automobiles, houses, paints and clothes. Although not generally realised, the production of industrial-type goods at the end of 1958 was approaching the former peak figure attained in 1956, whereas in some cases the demand for consumer goods was 20 to 25% below previous high levels. Since the life of many consumer goods tends to be short and the demand is particularly susceptible to stimulation by cleverly advertised new features, a rapid recovery in this field is anticipated in the 1959 to 1960 period. In turn, this should result in a demand for chemicals that ought to exceed considerably the general growth rate for industry as a whole.

An important guide to the immediate strength of the U.S. chemical industry can be obtained by comparing in typical cases the money spent in recent expansion programmes with total capital investments. For example, the greatest of the chemical giants, Du Pont, with a total plant investment exceeding $2000 million, spent $576 million of this sum during the last three years, which represents a 40% increase in capital outlay in this short period. Dow Chemical increased their gross plant investment by an even greater ratio; of a total of $1150 million, no less than $422 million were spent in the last 3 years, a 58% expansion.

A tabulation of such vast sums brings a realisation that, in the eyes of the stockholders, the main products of the industry are dividends and the by-products are chemicals. Furthermore, the future earnings potential of the industry must be very bright, otherwise the prime raw material—money—would never be available from outside sources in such a copious flow. An increasing number of concerns appears to be giving up the struggle of financing growth solely from recycled earnings and the response from insurance companies, mutual funds, banks and the public is evidence of confidence in the U.S. chemical industry.

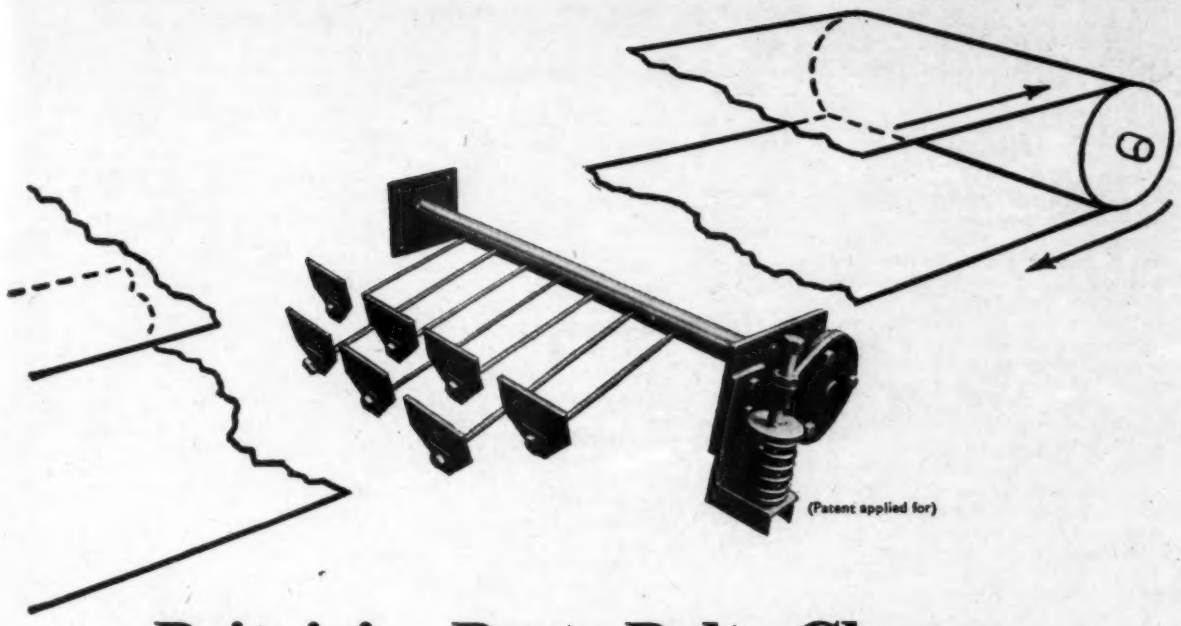
The Price Factor

In addition, a major factor likely to affect future earnings are trends in selling prices, since a rising turnover will not bring a proportionate increase in profits if the market is weakened by excess plant capacity. Based upon data from the U.S. Bureau of Labour Statistics, and taking the 1947 to 1949 period as 100, the price increase of all industrial products was 32% in 1957, while the price increase figure for industrial chemicals was about 25% in the same year.

An inspection of price increases for the principal divisions of the chemical industry shows some features of importance to investors and consumers alike. Taking the period 1947 to 1949 as 100, the per cent increases by October, 1957, were 138.6 for inorganic chemicals, 116.3 for organic chemicals, 108.8 for plastic materials and 107.6 for fertiliser materials. In 1958, these figures were 140.3, 115.5, 105.4 and 106.3 respectively. Undoubtedly, improved processes and cost reduction campaigns in the petrochemicals, plastics and fertiliser fields were responsible for part of the price reductions, but the well-known temporary over-capacity in certain fields, such as polyethylene, ammonia and formaldehyde is likely to be a significant factor.

The policy of increasing plant capacities and installing new or modernised equipment to meet future output levels is not without risk in the chemical industry, since a process may be rendered obsolete quite suddenly by new developments. However, it is generally felt that a company with extra capacity and up-to-date facilities to meet future demands is a much better source of investment than a concern which has not expanded or modernised at all, even though the share-price-to-earnings ratios may be comparable. Those companies which have either related or diversified interests in several chemical fields together with instant extra capacity should be in a very strong earnings position during the expected recovery period ahead.

BCE 6137 for further information



Britain's Best Belt Cleaner

EFFECTIVE—AND SIMPLE!

Consisting of small blades, each mounted on a spring steel bar, the *Multi-Blade Scraper* overcomes all the disadvantages associated with the normal counter-weighted devices.

LONGER BELT LIFE

The new *Multi-Blade Scraper* keeps conveyor belts permanently clean and ensures mechanical efficiency by eliminating carriage of harmful abrasive waste.

DOUBLE CLEANING

The bars are mounted at slightly greater pitch than the width of each blade, and by using bars of different lengths, it is possible for most of the belt to be scraped twice at each pass.

MOST ADVANCED DESIGN

Each blade is fitted with wear resistant rubber. The cleaning efficiency is very much greater than by any other system yet devised.

EASE OF BLADE REPLACEMENT

Maximum blade life is ensured by exchanging the positions of inner and outer blades before the inner blades wear excessively. This operation can be carried out by the removal of a single nut for each blade.

Please write for further details quoting ref: BCE 43

Sutcliffe — *BRITAIN'S BEST CONVEYORS*

RICHARD SUTCLIFFE LTD
HORBURY · WAKEFIELD

dm RS43

World of Chemicals

Expanding Rumanian Chemical Industry

Reflecting the greater output and wider range of products from the Rumanian chemical industry are some of the figures for exports published by the foreign trade organisation, Chimimport. According to the information published, exports of caustic soda last year were six times greater than in 1955; over the same period the quantities of soda ash increased twelve times and carbon black doubled. Among the materials which are now available in bulk are carbon tetrachloride, which is produced by the direct chlorination of methane, calcium carbonate, sodium bicarbonate, sodium silicate and many others. Fine chemicals such as acetylsalicylic acid and salicyclic acid are also exportable.

Many of the chemical products in this country are produced at a large works at Turda, which recently had two extensions under construction. Both are now in production, the one for the manufacture of carbon tetrachloride from methane, and the other for the production of benzenè hexachloride by photochlorination. The output of the latter plant is expected to be around 700 metric tons of gamma isomer per annum.

In another part of the country, at Timisoara, a new plant recently came on stream for the manufacture of phthalic anyhdride, but so far no details have been released either on the output of the plant or the nature of the process taking place within it.

New Montecatini Ethylene and Propylene Plant

A new Montecatini 30,000 metric-ton-per-year ethylène plant, engineered by The M. W. Kellogg Co., New York, and Kellogg International Corp., London, has just been placed on stream. This is Montecatini's second ethylene plant in Ferrara; the first, also a Kellogg plant, went on stream in 1955.

The new plant is designed to produce 30,000 metric tons per year of high-purity ethylene products (95-99.85% purity) and 15,000 metric tons per year of high-purity propylene product from the pyrolysis of light naphtha or from the pyrolysis of heavy naphtha.

The pyrolysis section of this plant has been designed to provide gum free operation. Each of the three parallel pyrolysis systems consists of a charge pump, naphtha preheat furnace, flash drum and pyrolysis furnace in addition to the steam and quench equipment. Separate lines from battery limits are provided to permit charging either light or heavy naphtha to any pyrolysis system. The addition of naphtha preheat furnaces allows low-pressure steam to be used in the pyrolysis furnace and reduces gum formation in the furnace vaporisation zones.

Downstream from the pyrolysis section is equipment for compression and hot fractionation, caustic scrubbing, drying, acetylene removal, cold fractionation, ethylene refrigeration and propylene refrigeration.

The high-purity propylene produced at the new Ferrara installation will go into the production of Montecatini's new "Moplen" isotactic polypropylene plastics, fibres and elastomers.

Esso Extend Petrochemical Plant in Cologne

In order to satisfy the rising demand of the chemical industry for chemical intermediates, Esso A.G. has set up a second steam cracker with working-up plants on its Cologne refinery site. The plant, the building of which requires 50 million D.M., will start production in the middle of 1961. With this the company will double the capacity of its plants for working-up petrochemicals.

The steam cracker, which was developed by Esso Research & Engineering Co., the research company of the Esso organisation, produces unsaturated hydrocarbons which are used as raw materials for further chemical working-up. The first steam cracker, which was completed this year in the Cologne Esso refinery, and the petrochemical plant belonging to it are now coming into operation.

Alongside large quantities of ethylene, propylene, butadiene and butylene, they are producing methane and hydrogen as well as higher boiling liquid products. A large plant is planned for the production of tetrapropylene for supplying the German detergent industry with raw material for the production of synthetic detergents. At the moment German industry is dependent on the import of such raw materials. The products of the Cologne petrochemical plant will be supplied through pipelines, tank wagons and in storage tanks to the chemical industry. Some important customers of the various products are situated in the immediate neighbourhood of the Cologne refinery.

Chemical Developments in Rhodesia

A pilot plant, designed to prove that phosphate in the apatite deposits at Darowa, near Inyazura, Southern Rhodesia, can be mined and used in the manufacture of superphosphate, is being constructed by Darowa Minerals Ltd., a subsidiary of African Explosives & Chemical Industries (Rhodesia) Ltd., at a cost of £70,000. If the project, which it is estimated will cost £100,000, is a success, reports Barclays Bank D.C.O., it will no longer be necessary to import phosphate rock from Morocco at a cost of some £700,000 each year.

Also under construction by African Explosives & Chemical Industries (Rhodesia) Ltd. is a new plant to manufacture aluminium sulphate, used for water treatment. At present, about £50,000 is spent each year on importing this chemical. Production in Rhodesia is expected to commence this year.

Fisons Expand in Canada

The formation of a new fertiliser company represents an important westward expansion of Fisons fertiliser activities in Canada. Fisons and Albatros already own one Canadian company, International Fertilizers Ltd., founded in 1930, which operates granulating plants at St. John, New Brunswick, and Wolf's Cove, Quebec. The new company is in association with Albatros Superfosfaatfabrieken N.V., of Utrecht, with whom all Fisons overseas fertiliser companies are jointly owned.

The new company, Hy-Trous Co. of Canada 1959 Ltd., Cornwall, Ontario, takes over the assets and goodwill of a family fertiliser business, Hy-Trous Co. of Canada Ltd.

In the past the factory has mixed granular and powder raw materials, but an immediate stepping up in the production of better fertilisers is planned. The new company is installing a granulating plant to come into production this season.

The European parent companies are represented on the board by Mr. J. Watson Napier, a director of Fisons Ltd. and managing director of Fisons Fertiliser Division, and Mr. John D. Waller, managing dirtctor of Albatros Superfosfaatfabrieken N.V.

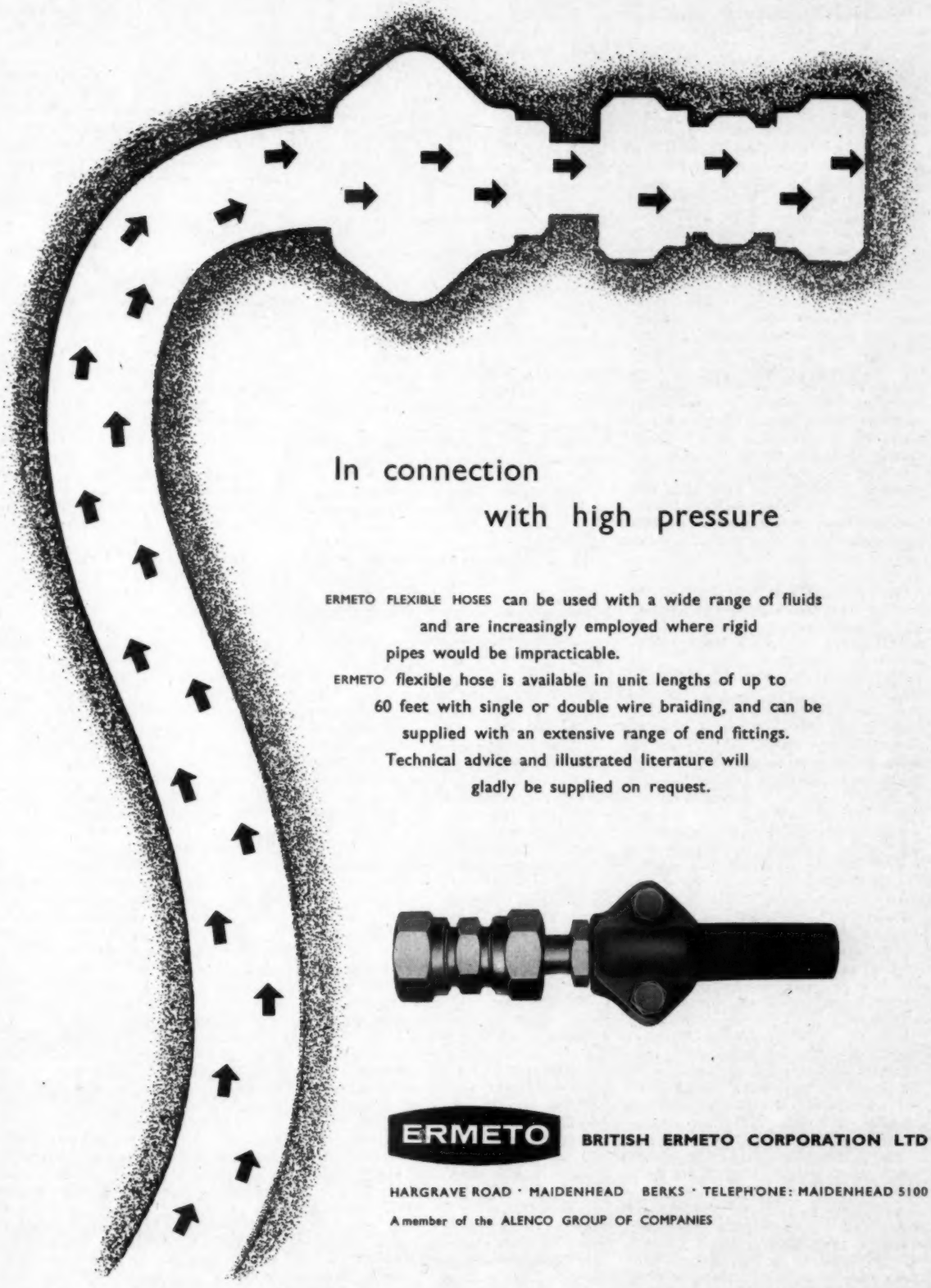
Contracts for Power Gas

The Japanese licensees of The Power-Gas Corporation Ltd., the Mitsubishi Chemical Machinery Manufacturing Co. Ltd. of Tokyo, have received an order for one unit of carburetted water gas plant, with a capacity of 2 million cu. ft/day, for the Saibu Gas Co. Four units each of similar capacity have previously been installed for the same company. The Japanese licensees have also received contracts for four gas producer units, each 10 ft 6 in. in dia., and for a CO conversion plant for the Toho Gas Co.

Earlier this year The Power-Gas Corporation (Australasia) Pty. Ltd—an overseas member of the Power-Gas Group of companies—received an order for one unit of C.W.G. plant with a normal capacity of 9 million cu. ft/day and with a peak load capacity of 12 million cu. ft/day. This plant is to be installed at the Mortlake Works, Sydney, of the Australian Gas Light Co.

Continental Manufacture of Catalysts

Universal-Matthey Products Ltd., an associate company of Johnson, Matthey & Co. Ltd. and Universal Oil Products Co., has formed a subsidiary company in Cologne, Universal-Matthey Products (Deutschland) G.m.b.H., with a nominal capital of DM 20,000. The object of this new enterprise is the manufacture of platinum catalysts to meet the needs of petroleum refineries employing the U.O.P. platforming process in Western Germany and the Common Market countries. Mr. L. C. Montague and Mr. F. O. Newton have been appointed members of the board of administration, and Mr. A. E. Richards has been appointed manager.



In connection with high pressure

ERMETO FLEXIBLE HOSES can be used with a wide range of fluids and are increasingly employed where rigid pipes would be impracticable.

ERMETO flexible hose is available in unit lengths of up to 60 feet with single or double wire braiding, and can be supplied with an extensive range of end fittings.

Technical advice and illustrated literature will gladly be supplied on request.

ERMETO **BRITISH ERMETO CORPORATION LTD**

HARGRAVE ROAD · MAIDENHEAD BERKS · TELEPH'ONE: MAIDENHEAD 5100

A member of the ALENCO GROUP OF COMPANIES

Book Reviews

Introduction to Chemical Engineering
by Charles E. Littlejohn and George F. Meenaghan
Reinhold Publishing Corp., New York, Chapman & Hall, London, 1959, 271 pp., 63s.

AN ever-present problem in teaching a technology is to ensure that the student has a thorough understanding of the elementary principles of chemistry, physics and mathematics, upon which his future professional subjects are based, and at the same time is able to relate these scientific studies to the technological material of his chosen career. In the past, chemical engineering courses tended to begin by concentrating in the first year on chemistry and mathematics, adding some engineering in the second year and providing the bulk of the instruction on chemical engineering in the third year. It is now realised that this is not an altogether satisfactory scheme, and most courses now provide instruction in what would be regarded as purely chemical engineering subjects side by side with the grounding in the fundamental sciences from the first year on.

It is evident from this book that this problem is also felt in teaching institutions in the United States, and one of the aims of this text is to provide elementary instruction for the student at the beginning of his chemical engineering course with a view to showing him the aims and scope of chemical engineering and the relation between the purely scientific and the technological aspects of the subject. It commences with a chapter on the profession of chemical engineering and introduces almost at the beginning the idea of the engineer as a professional man. The authors then give brief definitions of the so-called unit operations. Some of these definitions illustrate the difficulty of trying to describe ideas to a student who has little or no knowledge of the technology. For example, distillation is defined as the separation of liquid mixtures into relatively pure components by taking account of the relative volatility of one component with respect to the others. The more inquisitive student will now ask, "What is relative volatility?", but he will not find any mention of it in this book.

The second chapter is a useful introduction to the use of the library and chemical engineering literature. Again, the examples chosen are almost all in specialised topics in process engineering, which for their proper understanding require a reasonable knowledge of the technology. Generally, students do not use literature or reference books in the early stages of their courses, and this chapter, although useful, is perhaps superfluous in an introductory book.

The next three chapters on graphs and graph paper, process variables and molecular units demonstrate how far below the level of his English counterpart is the American student embarking on a university or college course.

The remaining chapters, from 7 to 13, are concerned with what are often called chemical process principles—that is, the solution of material and energy balances using simple physico-chemical laws. There is a short section on dimensional analysis, which again seems somewhat superfluous, as this subject is at least as conveniently treated when dealing with fluid mechanics or heat transfer. There is a brief chapter on economic considerations which is so short as to do little more than mention that they exist. The authors state that there are several good texts on this subject, but do not give any references to them. Finally there is an appendix giving physico-chemical data and a useful index.

This book is a somewhat remarkable mixture of chemical engineering and philosophy, school-level mathematics and moderately advanced material and energy balance problems. As an introduction to chemical engineering, only a few of the chapters are likely to be useful, and most of the material which links the physics, chemistry and mathematics to the technology of process engineering has been dealt with at least as well in two or three other texts. It is an interesting attempt to solve the very difficult problem of what best to give the student at the beginning of his course on chemical engineering, but it is felt that the attempt has not been completely successful.

D.C.F.

Chemical Processing of Nuclear Fuels
by F. S. Martin and G. L. Miles
Butterworths Scientific Publications, London, and Academic Press Inc., New York, 1958, 242 pp., 40s.

THIS monograph deals largely with the inorganic and physical chemistry of the fuel materials and fission products in nuclear reactors. The book was published in 1958, and included material which had been declassified no later than 1957. It is therefore wise of the authors to have concentrated on principles rather than aspects of technical detail. The emphasis is on basic chemistry and not on the chemical engineering aspects.

The book is divided into five sections. The first, "Nuclear Considerations", deals with the various chemical systems involved, the economics of fuel processing and the requirements of the processes. The following three sections enter into the processes involved; thus solvent extractions, ion exchange and precipitation are classed together under aqueous processes, while distillation of metals, liquid metal extraction and fluoride volatilisation and separations based on chemical reactions are grouped under non-aqueous processes. The third section deals with the disposal of radioactive effluents and their treatment with the recovery of fission products. The final section attempts to assess the future trends in processing with the changes in requirements with the development of power reactors rather than plutonium producers.

A certain dissatisfaction was felt while reading the book with its brief review style—perhaps the authors have attempted to cover too much ground in a restricted space, or perhaps the more detailed material is still classified. A critical evaluation of the material is largely left to the reader, who is presented with a well-organised summary. References are given after each section, and the book lacks a comprehensive author index. These minor criticisms must not be allowed to detract from the great value of the monograph; it is an excellent attempt to summarise a large and growing field, which will serve as an introduction of great value to many chemical engineers, particularly if they have had a comprehensive chemical background.

W. STRAUSS

Uranium Ore Processing
Edited by J. W. Clegg and D. D. Foley
Addison-Wesley Co. Inc., Massachusetts 1958, 450 pp., 60s.

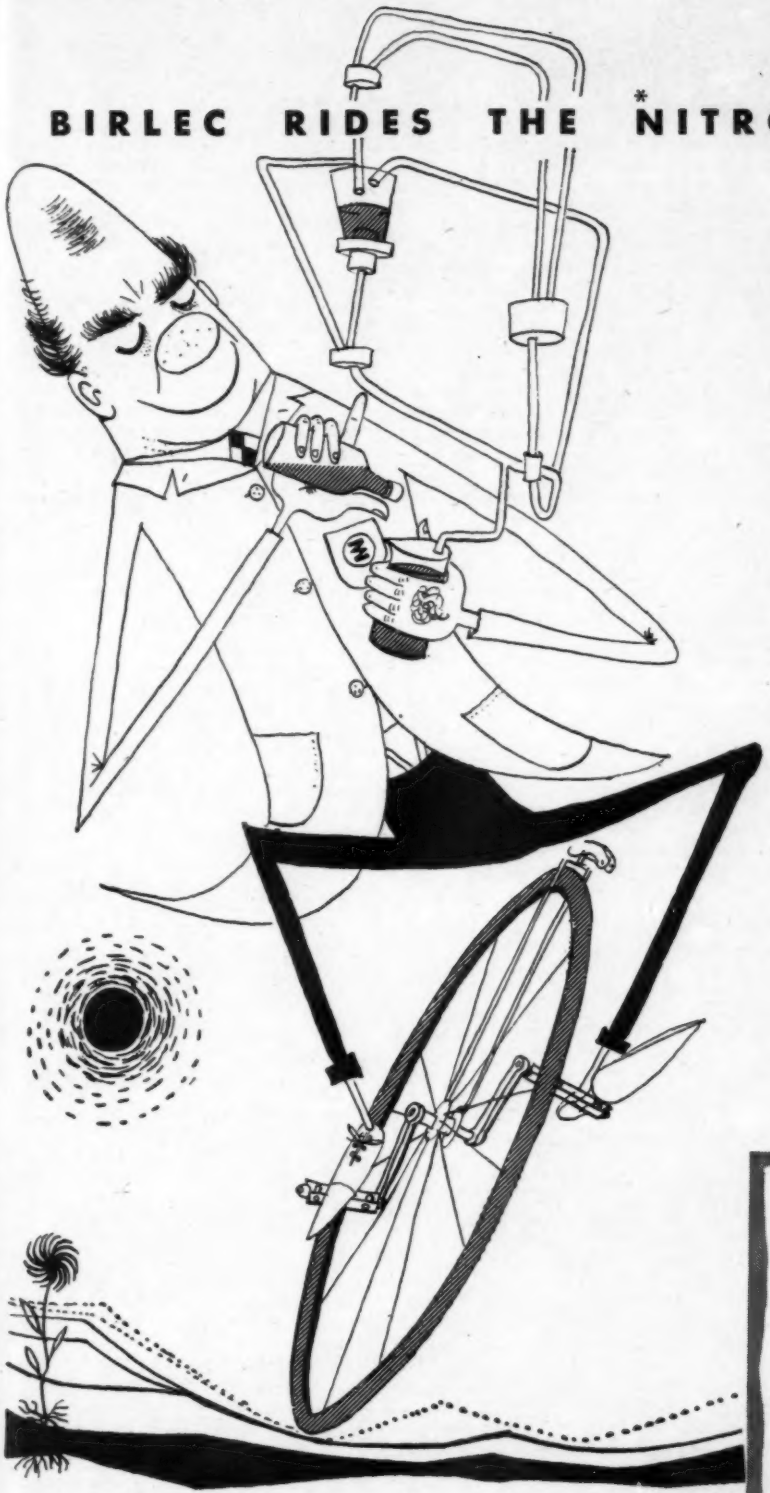
THE claim made by the publishers that this volume presents for the first time, a complete description of the winning of uranium from its ores, is fully justified and herein lies its true value, not only to workers in the field but to those also who have any interest in uranium production, or in the winning of valuable products occurring naturally in low concentrations from their associated minerals. Considerable praise is due to the editors. Each chapter has been contributed by one or more workers having particular knowledge and experience of a certain aspect of the subject and yet the work as a whole has an outstandingly high standard of consistency and readability. Every chapter concludes with a comprehensive list of references which emphasise the international interest in winning uranium, in addition to establishing the great amount of effort contributed by the U.S.A. Quite apart from its high technical value, the present work is a testimony to those who, starting practically from scratch, have established a major industry in considerably less than two decades.

The first four chapters consider the sources of uranium, its mining, analytical procedures and physical methods of concentrating deposits. The next five chapters cover chemical extraction and purification, and these are followed by two chapters which illustrate the operations by describing a number of actual installations. The final chapter discusses the particular problems associated with health and safety in the handling of uranium-containing materials.

Chemical engineering has, naturally, played a very large part in the successful development of the processes; consequently unit operations are discussed in considerable detail. Problems of solid-liquid separation are frequently as difficult in the initial stages of ore extraction as in any other process industry, and so emphasis is placed on the methods devised for conditioning slurries before separation. Then there are excellent descriptions of two operations, ion exchange and solvent extraction, whose widespread application to industrial processes in recent years owes much to the

BCE 6139 for further information

BIRLEC RIDES THE *NITROGEN CYCLE



We build nitrogen generators—and a wide range of other gas generators, too. The fact had better be stated quickly before the purists point out that the nitrogen cycle also concerns organic matter: no, we do not make nitrogen from decomposing animal tissue. Specially designed generators separate nitrogen from air by the combustion of fuel, which converts the oxygen content into carbon dioxide and water. We deal with these waste constituents, too, but one of our engineers will explain all that. Protective atmospheres for furnaces, including annealing of transformer laminations; purging of electric lamps and handling of semi-conductors; prevention of oxidation in chemical processes and in packing sensitive foodstuffs; handling of inflammable liquids in petroleum refining; all these processes employ nitrogen protection. Estimates of capital and running costs for Birlec nitrogen generators are available on request.

*. . . *if there were other gas cycles we'd ride those also, as we build generators for hydrogen, carbon dioxide, inert gases, and furnace atmospheres, in addition to nitrogen.*

Dryer and Gas Plant Division of
BIRLEC LIMITED
An A.E.I. Company
ERDINGTON · BIRMINGHAM 24 · Tel: EAST 1544

LONDON
SHEFFIELD
GLASGOW
NEWCASTLE-ON-TYNE
JOHANNESBURG

SM/B4995

Book Reviews (continued)

pioneering work carried out by uranium processing technologists. Both subjects are treated in such a manner that they are as valuable as general treatises as they are in their specific applications. The book is generously illustrated by flowsheets and flow diagrams, particularly in the final chapters describing actual installations.

The book is well presented. It contains a great deal of data of general interest in addition to fulfilling its specific function, and should have a very wide appeal since it fills a definite gap in technical literature.

G. K. DICKSON

Insulation for Small Transformers
by J. H. Mason and C. G. Garton
Electrical Research Association,
Report Ref. L/T381, 1959, Price 37s. 6d.

THIS handbook provides valuable guidance and data for designers of all forms of electrical insulation, and will be particularly useful for assessing the applications of new materials, and the insulation requirements, for onerous or unusual service conditions. Factors which affect the electric strength and the life of insulation in service are considered in some detail. Numerous graphs are provided showing the variation of discharge inception stress with the thickness and permittivity of insulation, both for surface discharges and for internal discharges in cavities of varying thickness. Mechanisms of breakdown by discharges in "solid" and in oil-impregnated paper insulation are described and graphs and tables illustrate the relative resistance to breakdown by discharges or surface tracking in some 20 different sheet and moulded insulating materials. The effects of varying the temperature and the insulation thickness are considered.

The electrical, thermal and mechanical properties of wire coverings, paper and fabric sheet insulation and laminates are presented in tabular form, and the merits of impregnation with oil, varnishes and casting resins discussed. The importance of complete dryness and of effective impregnation are emphasised.

The merits and significance of non-destructive tests, such as discharge detection and measurements of insulation resistance, loss angle and dispersion are compared with the customary over-voltage tests, which often give little assurance of satisfactory life in service.

Although largely based on experience at the Electrical Research Association, this pocket-size book presents data from many other sources, and 136 references are given.

Introduction to Thermodynamics of Irreversible Processes
by I. Prigogine
Charles C. Thomas, Springfield, U.S.A. and Blackwells Scientific Publications, Oxford, 1958, 114 pp., 34s.

PROFESSORS PRIGOGINE and DEFAY are well known for their extensive "Treatise on Thermodynamics", the third part of which, "Irreversible Phenomena", is still in preparation. The present booklet by the more senior author of the treatise may be considered as a preliminary to this; not comprehensive in itself, but a valuable introduction to the large number of phenomena which take place outside the equilibrium state. This includes all chemical reactions which proceed irreversibly.

The method followed is that of the school of Th. De Donder, of which the author is the leading member, and makes systematic use of the concept of the degree of advancement, or extent, of a chemical reaction. The first two chapters give the classical definitions in thermodynamics, and then the book goes on to discuss the production of entropy, which is the sign of an irreversible process. subsequent chapters describe the application of this principle to the phenomenological laws, such as heat flow and the Einstein diffusion law; and to chemical reactions—in particular consecutive reactions.

The book will be useful to those requiring leads when developing new thermodynamic techniques for irreversible systems, as it is likely to be several years before the full treatise is available in English. The treatment, however, is brief, and rather difficult to follow on a first, or even a second, reading, and the approach is not likely to appeal to the ordinary chemical engineer.

W. STRAUSS

Shorter Notices

Lehrbriefe für Kältetechnik
Numbers 11 to 15, DM 1.30 each + 1 Folder DM 21.0. 1958-1959. Verlag C. F. Müller, Karlsruhe.

WE HAVE EARLIER referred to the general scope of this excellent series of instructional notes for fitters and mechanics (March, 1959, p. 124). Publication now continues with fresh material in the field of basic physics, refrigeration technology and electrical technology. The series on technical calculation has been completed and this group includes the final sections on physics. Each Lehrbrief consists of 24 pages and a total of 30 of these is envisaged.

British Petroleum Equipment. 1959/60 edition. £2 10s. Council of British Manufacturers of Petroleum Equipment, London, S.W.1.

THE Council of British Manufacturers of Petroleum Equipment (C.B.M.P.E.) was founded in 1943 and has expanded to a present-day total of 450 member companies all engaged in one way or another in supplying equipment or services to the oil industry. This is the seventh edition of "British Petroleum Equipment" the first having been published in 1947. This edition is the largest to date and more than 300 members are represented in the catalogue pages. In the Classified List of Equipment and Services more than 2000 separate items of equipment are listed. In addition, this valuable reference book gives an outline of the work of C.B.M.P.E., lists its officers and names the membership of its committees.

The Structure of British Industry
A symposium edited by Duncan Burn.
Vol. I. Cambridge University Press, London, 1958, 403 pp., 45s.

THIS IS THE RESULT of a venture organised by the National Institute of Economic and Social Research. The chapters of this book cover industries responsible for 40% of total industrial employment and include a survey of the chemical industry. After treating the problem of definition, the author— W. B. Reddaway, Director, Department of Applied Economics, University of Cambridge—surveys the size distribution of chemical firms. Separate sections are devoted to sulphuric acid, alkalis, dyes and dyestuffs, and plastics materials. The study is backed by 13 tables of important relevant data including statistics.

Fire Research, 1958
Report of the Fire Research Board with the Report of the Director of Fire Research. H.M.S.O., 5s. 1959.

THE REPORT includes reference to explosions and flame arresters. It is stated that results enable prediction to be made of the behaviour of crimped ribbon arresters widely used in industry. Tests have also been made with arresters of perforated polyvinylchloride sheeting. Investigations are in progress to provide the necessary design data for explosion release for complicated duct systems.

British Standards

B.S. 1547:1959. Flameproof industrial clothing (materials and design). 3s.

B.S. 3119:1959. Method of test for flameproof materials. 3s.

B.S. 3120:1959. Performance requirements of materials for flameproof clothing. 3s.

THESE THREE related standards set out requirements with which articles of industrial clothing must comply before they may be called "flameproof", the performance requirements by which the flameproof qualities of materials may be judged and the method of test which is to be employed in assessing these performance requirements. They are linked with the new standard for "materials of low flammability"—mainly of domestic interest—in B.S. 3121. In this way, materials resistant to flame have been standardised in a much wider sense than heretofore.

B.S. 2995:1958. Cast and Forged Steel Valves Screwed and Socket-welding Size ¼ in. to 2 in. for the Petroleum Industry. 10s.

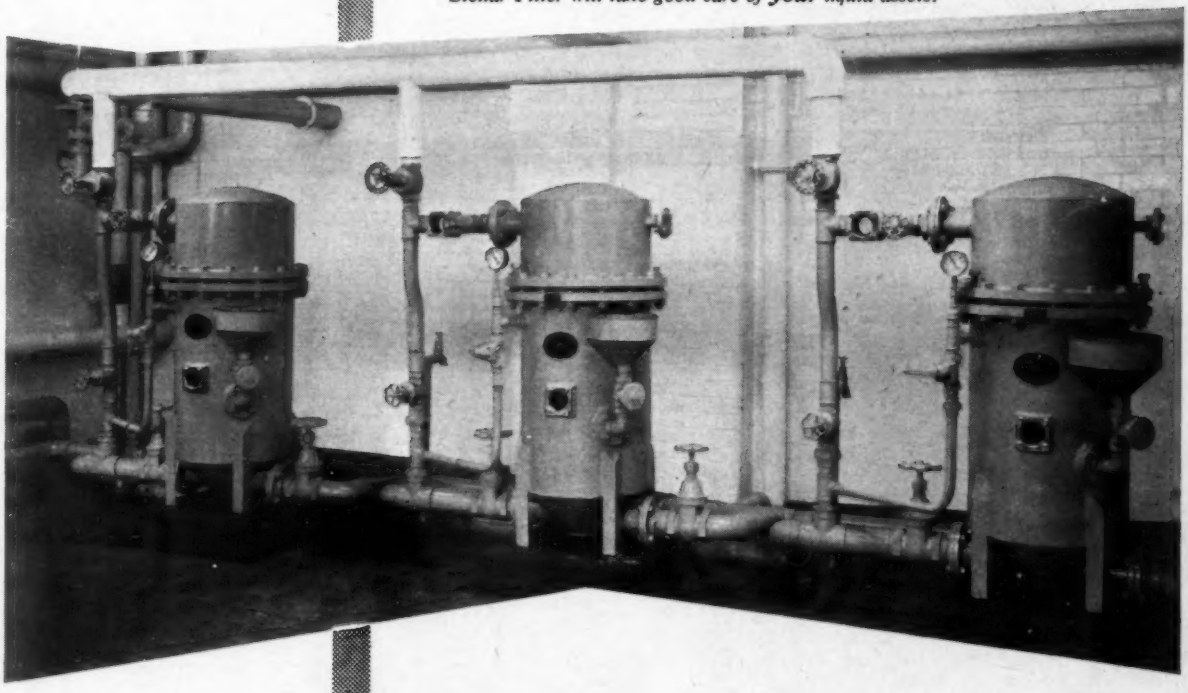
THIS IS ONE of a series of standards for valves prepared under the authority of the Petroleum Equipment Industry Standards Committee. In view of the international character of the petroleum industry, it was considered desirable that valves to this standard should, as far as possible, be comparable with similar valves produced by American manufacturers. In the preparation of this standard consideration has therefore been given to existing American practice.

BCE 6140 for further information

Safeguard your liquid assets*

Liquid assets in the shape of edible juices and industrial fluids, chemical solutions, oils and spirits, are too valuable to be wasted. They need the Stellar Filter to safeguard them, to render liquid loss almost negligible whilst clarifying and purifying. Designed to operate with supreme efficiency, the Stellar Filter has an unchokeable filter bed and is perfectly simple to control. It is remarkably economical, too, for it can be cleaned without dismantling or loss of liquid, and occupies very little ground area.

Tell us your problem and we'll gladly advise you how and why the Stellar Filter will take good care of ***your*** *liquid assets.*



* *They may be: WAXES — OILS ESSENCES—WINES—SPIRITS JUICES—CHEMICALS PHARMACEUTICALS SYNTHETIC RESIN SOLUTIONS SOLVENTS—VARNISHES INDUSTRIAL FLUIDS—and, of course, WATER.*

with the

STELLAR FILTER

...another **Paterson** *design for purity*

THE PATERSON ENGINEERING CO. LTD., 129 KINGSWAY, LONDON, W.C.2.

PLANT EQUIPMENT NEWS

Gyratory and Roll Crushers

Two designs of crushing machinery of French design have recently become available in this country.

The first of these machines is a gyratory crusher capable of giving a more constant degree of fineness of the crushed product compared with other machines of the same type. Known as the "Babbitless crushers", as the name implies, they do not use anti-friction metal as bearings. Instead, the entire mill relies upon roller bearings throughout. This feature results in a saving of lubricant and in maintenance costs, and at the same time high rotational speeds are possible. This, in combination with the small degree of eccentricity characteristic of the design, gives high capacity for a given size of machine. These machines, which are widely used for crushing ferrous and non-ferrous ores, limestone, etc., are available in a wide range of sizes. The primary machines have capacities based upon tough rocks of density 100 lb./cu. ft ranging from 6-5500 lb./hr and the installed horsepower varies from 12-600. The degree of fineness obtainable is from ¼-10 in. over the range of machines. The secondary machines are intended to finely grind and the outputs are somewhat smaller, ranging from 3 tons/hr to 330 tons/hr for final particle sizes of $\frac{3}{16}$ to 2 in.

In addition, extra heavy-duty double-roll crushers with manganese steel shells are now being produced. An important feature of this machine is that it can be fed with run-of-mine ores without any scalping arrangements. Experience has shown that this does not affect the capacity of the crusher and reduces considerably the cost of the feeding arrangements. **Babbitless Co. Ltd., 123 Victoria Street, London, S.W.1.**

BCE 6206 for further information

Lead Bricks for Atomic Shielding

A new lead brick for use in shielding personnel against gamma, beta and alpha rays has been produced by a special "pressure moulding" technique by British Lead Mills Ltd., A member of the Firth Cleveland Group.

The pressure-moulded lead bricks are produced in 2 in. and 4 in. thicknesses in the form of standard, corner, top and bottom bricks and also half or even quarter bricks which can be built up into a complete surround by virtue of their interlocking nature, to give the maximum thickness at any point of 2 in. or 4 in. or multiples thereof.

U.K.A.E.A., Harwell, have signed a two-year contract with British Lead Mills for these pressure-moulded lead bricks, which are adaptable for portable and permanent lead shielding for both commercial and for medical use. **British Lead Mills Ltd., Cleveland Row, London, S.W.1.** **BCE 6207** for further information

Large Heat Exchangers Used In Acid Recovery

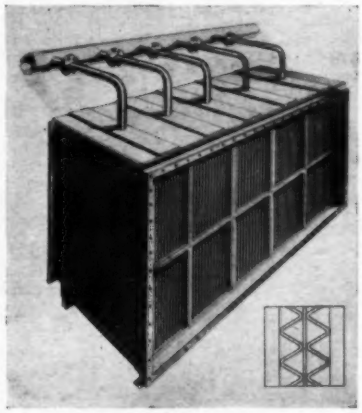
Three of the biggest Karbate impervious graphite shell and tube exchangers ever made are now in service in the plant of Olin Mathieson Chemical Corp., U.S.A. Operated vertically and in parallel flow with each other, the giant heat exchangers are used in the recovery of sulphuric acid from petroleum refining acid sludge. Approximately 400 gall. of treated cooling water a minute are required to handle a heat load of several million Btu an hour. The heat exchangers consist of an outer steel shell 45 in. (114.3 cm.) in diameter. In each shell are 685 impervious graphite tubes 12 ft (3.6 m.) long and 1¼ in. (3.18 cm.) in outer diameter for a total heat-transfer surface area of 2685 sq. ft (249.4 sq. m.) in each unit. **Union Carbide International Co., 30 East 42nd Street, New York, 17, N.Y., U.S.A.**

BCE 6208 for further information

Molecular Sieves

Jet aircraft fuel has a greater ability than petrol to dissolve water over a wide temperature range. Solubility of water increases with temperature. In addition, the fuel is often mixed with amounts of water above the solubility limit, either as an emulsion or as free and separate water. This can occur when water condenses inside storage tanks or when water is introduced during pumping operations. Molecular sieves are now being used to remove both dissolved and free moisture at the same time. **Linde Department, Union Carbide International Co., 30 East 42nd Street, New York, 17, N.Y., U.S.A.**

BCE 6209 for further information



Corrugated Plate Heat Exchangers

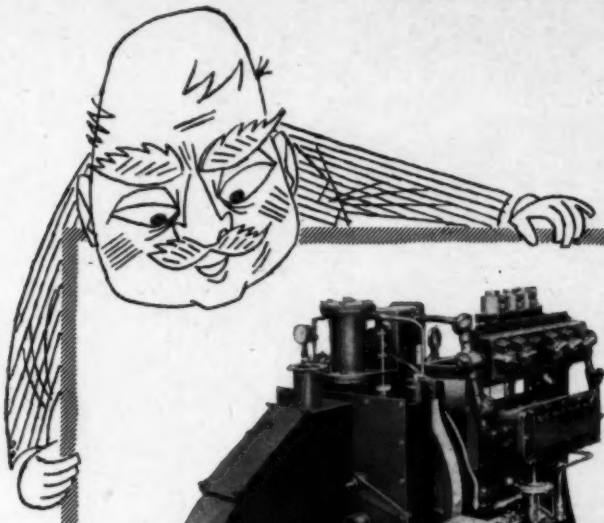
Heaters employing a corrugated plate matrix have been introduced recently by James Howden. The matrix itself consists of flat tubes or envelopes having fin surfaces both inside and outside in the form of corrugated material. Argon arc welding is employed extensively in the construction.

Usually this matrix is used in air heaters with steam as the heating medium, and the area per cubic foot of matrix volume is 111 sq. ft on the air side. The matrix can withstand a pressure of 2000 psig or more and is constructed of a special low-alloy steel known as Cor-Ten (Cu 0.25-0.55, Si 0.25-0.75, Cr 0.3-1.25, Ni 0.65 max.). Normally an air heater employing this type of extended surface will consist of several identical packs operating in parallel, an arrangement which ensures the simplest condensate and air venting arrangements. The sections can be removed from the casing without disturbing one another, a feature which is important for servicing. Apart from its use for preheating boiler combustion air, the heater may be used for supplying air to driers and as an air-operated condenser. **James Howden & Co. Ltd., 195 Scotland Street, Glasgow, C.5.**

BCE 6210 for further information

New Sharples Super-D-Hydrators

in the world's most complete range of centrifuges



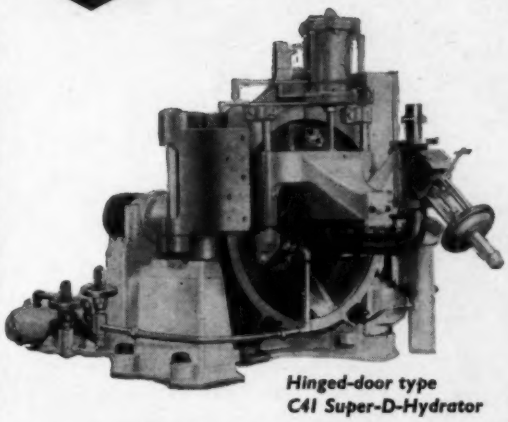
Even before the latest additions, Sharples was the most complete range of centrifuges in the world. Now it's better than ever, with brand new models of Super-D-Hydrator.

What do the new models mean ? The unique design features of the Super-D-Hydrator are of course retained. High centrifugal force, and completely automatic and continuous operation, continue to supply a solid foundation for the new designs. To these basic characteristics are now added increased capacities and ready availability for inspection, together with the refinements of totally enclosed operation for toxic hazardous materials. Antibiotics can be handled most successfully in a sterile version of the D-Hydrator, while special arrangements can be made for operation at either very high, or very low temperatures. Add up all these designs, and there's a properly tailored answer for every problem of crystal dehydration.

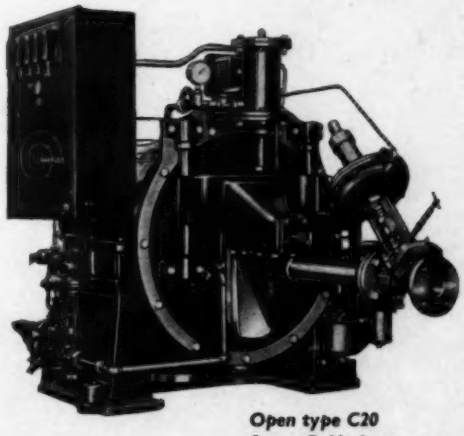
To Sharples world wide experience of some 2500 D-Hydrator installations is now added greater flexibility of operation through the application of careful detailed design, which is the hall-mark, " Sharples."

If your problem is the separating, washing and dehydration of any sort of crystal, and you desire consistency of product, combined with automatic and continuous operation, then you are invited to write to the address below or 'phone Camberley 2601 and talk it over with Graham Jackson.

Enclosed type C27 Super-D-Hydrator



Hinged-door type C41 Super-D-Hydrator



Open type C20 Super-D-Hydrator

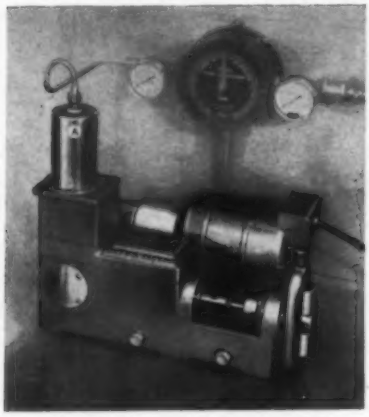
SHARPLES

SHARPLES CENTRIFUGES LTD., TOWER WORKS, DOMAN ROAD, CAMBERLEY, SURREY. *Telephone: Camberley 2601*

PLANT EQUIPMENT NEWS

Automatic Metering Pumps

A new range of metering pumps can be operated with *p*H, temperature, flow and other controls. Known as the DCL "M" pumps, they are responsive to pneumatic signals of from 3 to 15 psig, adjustment of the plunger stroke being carried out by a small, compact bellows motor operating through a mechanism designed to reduce "hunting" Available with different plunger sizes giving a range of capacities from 0-750 cc/hr to 0-37.3 lr/hr, the pumps are suitable for working pressures up to a maximum of 2400 psig, the maximum pressure depending upon capacity. The output from each pump is proportional to the air



pressure, the control gear being designed to give maximum capacity at either 3 or 15 psig.

Pump heads are interchangeable, the head in each case being easily removed and replaced by one of different capacity. Power is provided by a 1/15-hp totally-enclosed induction motor. The suction and delivery valves, both of which are duplicated, are of 12% chromium non-corrodible steel balls specially lapped to ensure high volumetric efficiency. Valve bodies, seats and the valves themselves can be readily removed by merely slackening one set screw to facilitate inspection and maintenance. As with other types of DCL "M" pumps, hydraulically-operated diaphragm heads are available for applications where it is desirable to avoid having glands in contact with the liquid being pumped. This is especially useful in cases where noxious fluids are being handled or when sterile conditions are required. **Distillers Co. Ltd., Great Burgh, Epsom, Surrey.**

BCE 6211 for further information

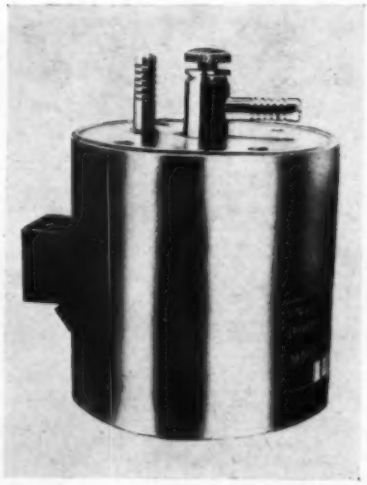
Ultrasonic Homogeniser

The principle upon which the Minisonic Model 3 ultrasonic homogeniser works is that of the liquid whistle (covered by British Patent No. 695,491 and many foreign patents). The arrangement of Model 3, the company states, permits four distinct methods of use: (a) gradual emulsification, which is particularly useful when the proportion of disperse phase approaches the theoretical limit or when there is danger of reversal in the emulsion system; (b) instantaneous emulsification, which will result in a continuous production process; (c) one-pass homogenisation for sonification of premixes; and (d) multiple transfer for emulsions and organic dispersions which yield better results when they are sonified more than once. All parts in contact with the liquid to be sonified are made in 18/8 stainless steel and corrosion-resistant materials. All surfaces are polished, which assists in cleaning; if necessary, the whole unit can be quickly dismantled. Built-in glass vessels and a three-way finger-tip control valve make for ease of operation and the Minisonic is supplied ready for plugging into a 15-amp, three-pin socket. **Ultrasonics Ltd., Otley, Yorks.**

BCE 6212 for further information

Small Industrial Pump

A new pump by Singleton is basically a vibrator type of miniature size which can be set to give a desired performance. The pump can be supplied in either a metal or bakelite cylindrical case, the overall dimensions of the metal-case model being 2½ in. long by 2⅝ in. diameter and weighing 24 oz. This model is designed for inclusion in scientific or engineering equipment. The bakelite model is 3½ in. long by 3½ in. diameter and weighs 30 oz., and was principally designed for use in bench work. There is a wide range available to give positive



or negative pressures in closed or open circuits. They are suitable for liquids or gases, including corrosive gases. Inlet and outlet connections and mountings can be adapted as required and the pump is supplied for A.C. voltages from 24 volts upwards. The pumps are produced to the individual requirements of each customer upon informations supplied as to the performance required. **Singleton Bros. (Instruments) Ltd., Effingham, Surrey.**

BCE 6213 for further information

Stiff Mesh

Expanded Metal have extended their range of mesh materials available to engineers and designers by introducing what they state is the first high-density polyethylene mesh. This mesh, produced in roll or sheet form and similar to metal mesh, is made from Rigidex polyethylene supplied by British Resin Products and offers many distinct advantages. It has a very low specific gravity (0.96) and is thus only one-third the weight of a corresponding aluminium mesh and less than one-eighth the weight of mild steel. In all thicknesses the mesh is flexibile enough to be handled easily, and in thicknesses above ¼ in. it is sufficiently stiff to be self-supporting. The mesh has a comparatively high strength to weight ratio and is virtually indestructible. It is resistant to water, sea-water, practically all chemicals, and to most oils, greases and solvents. The inertness of the polythene from which it is made means that very few substances will adhere to it, even temporarily, and the mesh is thus easy to clean. It is available in several colours which are inherent in the polyethylene, and therefore requires no painting or finishing. Besides having outstanding electrical properties, the mesh can be used at temperatures up to 100°C without significant distortion; thus they can be sterilised in boiling water if required. **Expanded Metal Co., Burwood House, Caxton Street, London, S.W.1.**

BCE 6214 for further information

Standardised Flow Meters

A series of Rotameters is now available in which metering tubes and floats are made to such a degree of interchangeability that, for many applications, individual calibration is no longer necessary. In this series, designated "Metric", the flow scale is engraved not on the metering tube but on a separate plate. Thus by replacing the scale plate another fluid can be metered. The series is based upon eight sizes of metering tube. For each of these, standardised floats are available made of 18:8:3 stainless steel, or anodised light alloy for air and non-corrosive gases or, alternatively, of ceramic material for certain corrosive

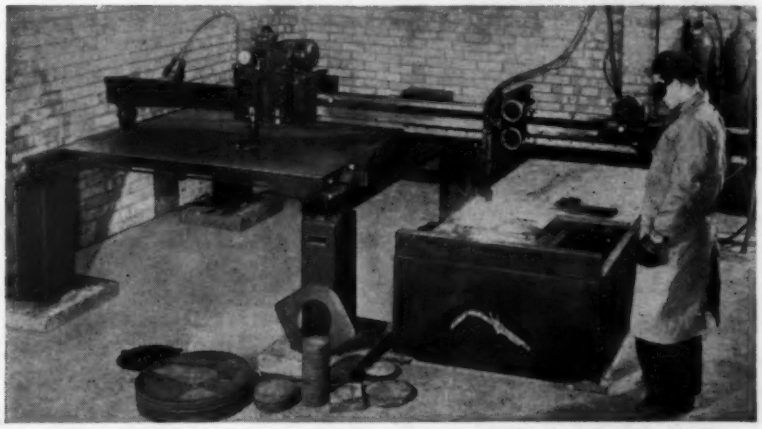
DENSO protection for *STRUCTURAL STEELWORK*

WINN & COALES LTD

DENSO HOUSE · CHAPEL ROAD · LONDON S.E.27

TAYLOR

stainless steel plate profiling ✳ **makes life easier!**



Write, call or phone. Our Area Manager will be pleased to call and discuss your needs.

✳ IMMEDIATTE CAPACITY
quick reliable service

ANY SHAPE, SIZE OR THICKNESS
we work directly from your drawings, no templates needed

LATEST PATENTED CUTTING PROCESS
Cut face needs no machining before welding

LARGE PLATE STOCKS available at mill prices

HIRE WORK Your own stainless steel cut

TAYLORS *ALSO PROVIDE SERVICE IN*

BAR BLANK SAWING
up to 14″ in dia.

BAR GRINDING
from ¼″ to 2″ dia.

SHEET POLISHING
10—24 swg. up to 10′ x 4′

TUBE POLISHING
from ½″ to 2½″ dia.

Ask for your copy of the TAYLOR STAINLESS STEEL priced stock list— new every 60 days.

TAYLOR STAINLESS METALS LTD. A.I.D./A.R.B. approved

Buckingham Avenue · Slough · Bucks. Tel: Slough 23951 Midland Sales Office: 63 Temple Row, Birmingham 2. Tel: Midland 1430/4610

BRITAIN'S PRINCIPAL STAINLESS STEEL STOCKHOLDERS

WPS-24

PLANT EQUIPMENT NEWS

liquids and gases. In this series the floats do not rotate, since there is no fluting of the head.

Each tube carries a fused-in reference scale graduated in millimetres; this forms the datum for the separate flow scales. If it is necessary only to ensure that a flow is held constant, the reference scale alone may be adequate. Every instrument is accompanied by a curve which correlates the reference scale with flows of air or water, and engraved scale plates for air and water in each size are available from stock. Scales for other fluids can be supplied at short notice.

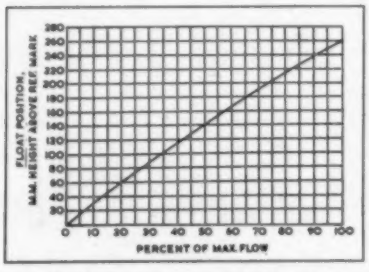
For users who prefer to calculate their own scales, a set of charts can be supplied, provided that the density and viscosity of the fluid are given.

This series is described in publication RP2020/1 of the **Rotameter Manufacturing Co. Ltd., Croydon.**

BCE 6215 for further information

Standardised Flowrators

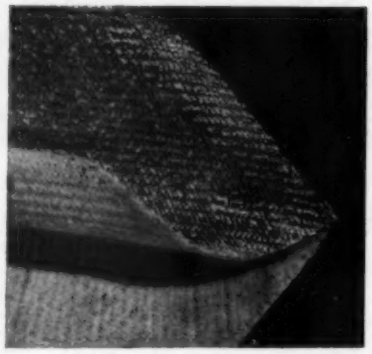
For Flowrator metering tubes the flow characteristics can be defined by one master calibration (see attached graph). This provides standardised true flow scales with a guaranteed accuracy of ±2% of maximum flow. It is thus possible to stock a range of instruments covering maximum flows from 12-2100 gph of water. The tubes used are standard 10-in. bead guided tubes scaled in actual flow units of 10-100% full-scale flow. Four standard floats are used for each tube size which give full coverage of the flow ranges with reasonable range increments. The flow of fluid passing through one of these meters is determined by multiplying the scale reading by a multiplying factor. Tubes and floats are interchangeable within the same meter size.



These instruments are supplied having a standard percentage scale tube and an attached metal scale marked for the particular fluid flow range being metered. Included in the range are instruments using preferred ceramic transfer scales which are based on the master calibration curve. The use of preferred ceramic transfer standard scales still achieves a good degree of standardisation whilst permitting an instrument to be manufactured with a direct flow scale on the metering tube itself. When an order is received for this type of instrument, the nearest preferred standard scaled tube is chosen which will cover the range and fluid being metered. The float is then individually designed to give a maximum reading equal to the full-scale flow being metered.

Details are available from **Fischer & Porter Ltd., Salterbeck Trading Estate, Workington, Cumberland.**

BCE 6216 for further information



Aluminium Asbestos Cloth

Turner Bros. have announced an addition to their extensive range of woven asbestos cloths, among which several qualities are now available having a coating of bright and highly reflective aluminium. These special fabrics should prove of interest to those concerned with thermal insulation problems. **Turner Bros. Asbestos Co. Ltd., Rochdale, Lancs.**

BCE 6217 for further information

Water Deioniser

The new "Loughborough" water deioniser, Model XD/2, incorporates a cartridge coated in black nylon which ensures a substantial increase in its life by providing improved resistance both to chemical and mechanical wear. The deioniser base is fitted with a non-slip tripod stand to give greater stability where the unit is used on the bench or in any unfixed position. **Loughborough Glass Co. Ltd., Loughborough, Leics.**

BCE 6218 for further information

Oil-free Compressor

In a number of industries where compressed air is used, one of the principal requirements is that the air should be completely oil-free. Food preparation, confectionery and certain chemical processes have this problem. The WNO-112 compressor produced by Joy-Sullivan provides one answer to the problem. It is a special version of the popular WN-112 two-stage, double-acting, water-cooled compressor. Air capacity ranges from 400-850 c.f.m. Of V-vertical construction, the compressor requires a minimum of floor space, while provision for a flange-mounted motor assists to keep down space requirements. The WNO-112 has carbon graphite piston bearing and sealing rings in place of oil lubrication in the cylinders. Long-rod construction with carbon-graphite piston rod/crankcase packing and baffle to guard against oil creep ensures that the air delivered is completely free from oil contamination. **Joy-Sullivan Ltd., Air Power Division, 7 Harley Street, London, W.1.**

BCE 6219 for further information

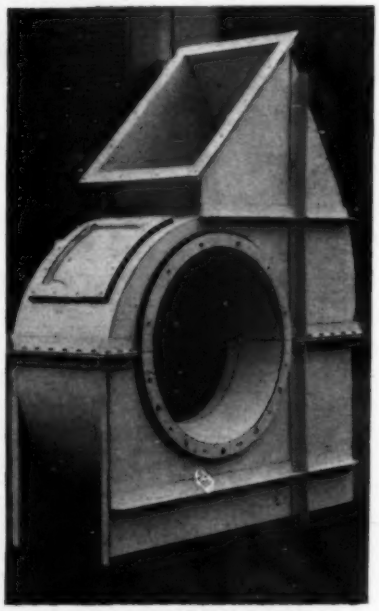
Hose Fittings

Among the wide range of Hercules hose fittings are a new lug-type coupling for suction and delivery hose and many other fittings for pneumatic, oxy-acetylene and all industrial hose. Hercules fittings are said to provide a unique gripping action due to special claw jaw grips which are fixed simply by hammering down, yielding an efficient joint, strong enough to withstand high pressure and dripless. **Newton Sales Co. Ltd., 517/523 Fulham Road, London, S.W.6.**

BCE 6220 for further information

P.V.C. Fan Casings

Manmil Plastics have introduced a range of fan casings constructed of high-strength P.V.C. They state that this type of plastics fan is suitable for use with most acids and alkalis working in temperatures not exceeding 140°F. In certain important parts the fan embodies the use of steel strengthening pieces which have been completely covered with



a heavy coating (baked on) of liquid P.V.C., and all internal screws are of nylon. Our illustration shows a typical fan casing measuring 7 ft 6 in. in height with an inlet of 30 in. in diameter. Fans having inlet diameters from 7 in. up to 40 in. can be supplied, state **Manmil Plastics Ltd., Castle Street, Stalybridge, Cheshire.**

BCE 6221 for further information

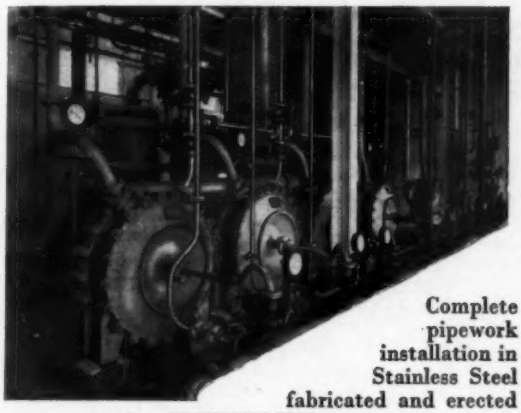
Analysis Decameter

A newly-developed test apparatus has been announced based on dielectric measurements. Its high sensitivity and exceptional accuracy are demonstrated

BCE 6144 for further information

Stainless Steel . . .

tanks, coils and pipework by *Jenkinsons*



Complete pipework installation in Stainless Steel fabricated and erected on site by JENKINSONS.

Also fabricated and erected on site by JENKINSONS, Stainless Steel ducting 9 ins and 18 ins dia. with special smooth finish both internally, to minimise friction losses, and externally, to improve corrosion resistance.

W. G. JENKINSON LTD.
ARUNDEL STREET; SHEFFIELD 1.
Phone 27438/9

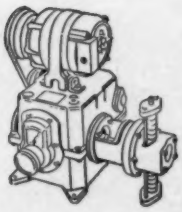
BCE 6145 for further information

Human pump's working day!

Nothing in nature works harder than the heart. Today and every day, your heart will pump 8 tons of blood through literally thousands of miles of tubes—yet it is no bigger than your fist.

Considering their remarkable performance, some of our Metering Pumps are relatively small and compact. They are astonishingly versatile, too. In our Metripump range, for example, there are models fitted with steam jacketed pump heads, high pressure liquid sealed glands, or pump heads made in special materials, where the length of stroke can be varied from zero to maximum, either whilst the pump is in operation or at rest. And every model backed by a first-rate After-Sales service. Our Sales Representatives can service on the spot any pump in our range. We are sure that our Publication 101 will interest you. Ask us for a copy.

Metering Pumps Limited



21, The Mall, Ealing, London, W.5. Telephone: EALing 4024 (PBX)
Telegrams: Metripumps, London, W.5
Cables: Metripumps, London.

PLANT EQUIPMENT NEWS

by decametric determinations on two commonly-employed solvents which in their pure state have dielectric constants which are quite close to one another.

Substance	*Dielectric Constant*	*Scale Reading*	*Temp. °C*
Cyclohexane	2.020	300	20
Benzene	2.284	492	20

The difference in the dial readings is thus about 200 scale divisions, which identifies the two compounds and establishes their purities. A practical application of the determination of the water content, using tetrahydrofuran as the test substance, yielded the following results showing the suitability of the decametric technique to rapid water-content determinations.

Substance	*Scale*	*%H_2O*
Tetrahydrofuran	548	0.0
	567	0.1
	674	1

The instrument has been developed by **Wissenschaftlich-Technische Werkstätten, Weilheim, Upper Bavaria.**

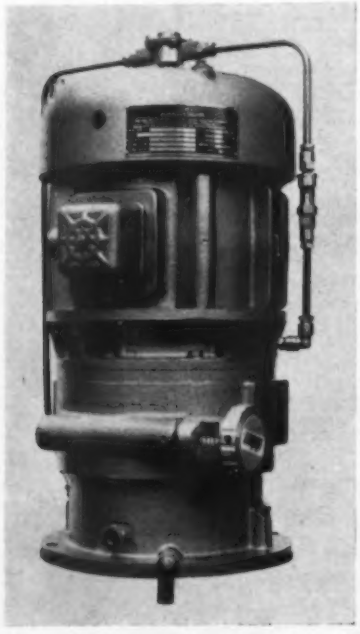
BCE 6222 for further information

New Vertical Variable-Speed Gear

Allspeeds Ltd, of Accrington, manufacturers of the Kopp variable-speed gear (the gearless gearbox), have now produced a modified version of the Kopp Variator which has been specially designed for vertical mounting. Hitherto, due to the splash method of lubrication, the standard model has only been suitable for mounting horizontally.

These units are ideally suited to stirring and agitating applications, particularly in the food and chemical industries.

The new unit has a separate oil sump casting located on the lower flange of the Variator. The necessity to use oil seals on the lower shaft has been overcome by incorporating a labyrinth and flinger arrangement which cannot deteriorate in service or allow oil to leak down the shaft.



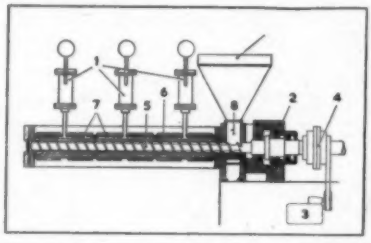
The oil is circulated from the sump into the upper bearings of the Variator by means of a pump which is driven by the upper shaft of the electric motor. The working parts of the unit are thus fully lubricated.

At the moment the size is limited to between ¼ and 5 hp with standard stepless speed variation over a nine to one output speed range. The unit illustrated can be supplied with either 960- or 1440-rpm motor giving output speeds of 320-2880 and 480-4320 respectively. Lower output speeds are obtainable by fitting flange-mounted reduction gears to the output shaft of the gear unit. **Allspeeds Ltd., Oakenshaw Works, Clayton-le-Moors, Accrington.**

BCE 6223 for further information

Vented Vapour-cooled Extruders

Available from the same company is a series of extruders fitted with vents for the removal of volatiles. These electrically-heated machines have length: diameter ratios of up to 36:1 and for temperature control are provided with a special vapour cooling system which operates in conjunction with an electronic temperature controller. These machines have two screws connected together to form one long screw with a decompression zone beneath the barrel vent where the two sections are joined together. The output of the two screw sections must be balanced and operating conditions are sometimes critical if material is to be prevented from extruding through and blocking the vent. A novel screw design has been developed to minimise this effect. Extruders can also be supplied with a connection for vacuum extraction at the vent and with an adjustable valve at the end of the screw. **Bone Bros. Ltd., Manor Farm Road, Alperton, Wembley, Middlesex.**

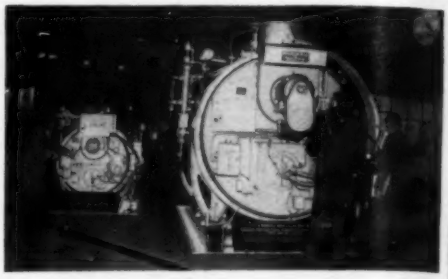


BCE 6224 for further information

Spectrum Analyser

For the Scottish Industries Exhibition to be held in September, 1959, James Scott & Co. have selected their Spectrum Analyser Type 190 as a major exhibit. This instrument is said to represent a major breakthrough in analyser techniques for the audio to supersonic frequency range. Operating on the superheterodyne principle with a highly selective "flat-topped" I.F. response which, in the standard instrument is 70 c/s wide, this instrument enables single frequency, or alternatively noise signals, to be measured accurately at input levels down to 1 microvolt, or even less. An oscillographic panoramic display allows the general nature of any spectrum within the frequency range of the equipment to be examined rapidly and a built-in thermocouple instrument permits the accurate measurement of noise powers at any required frequency. **James Scott & Co. Ltd., 68 Brockville Street, Glasgow, E.2.**

BCE 6225 for further information



Packaged Boilers

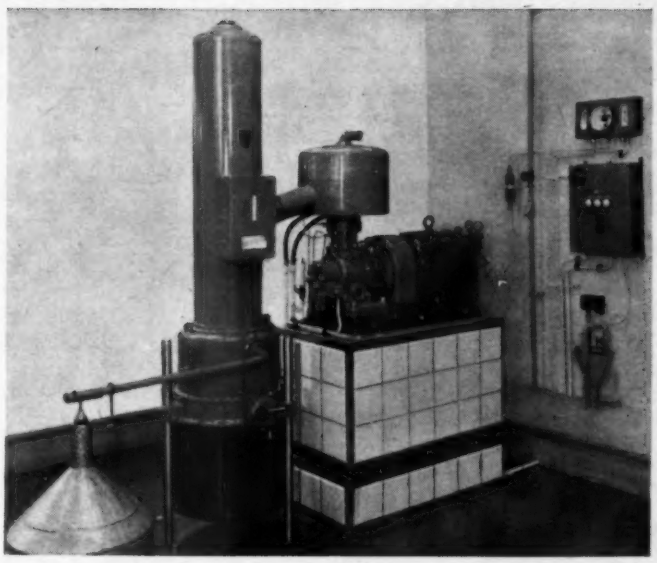
Packaged boilers of the Cleaver-Brooks design are now being manufactured in this country by the Marshall Organisation. In the accompanying photograph, taken at a recent exhibition, the large boiler on the right, a Model CB350, has an evaporation rate of 12,000 lb. per hour while the smaller boiler has a capacity of 1725 lb. per hour (model CB50). Both these models have a 150 psig working pressure. The CB type boilers now available have capacities ranging from 1380 lb. per hour to 20,700 lb. per hour for a working pressure of 150 psig. Higher pressure boilers can be made to order. In addition, the company can supply smaller Cleaver-Brooks boilers—the M type, also with a 150 psig working pressure, with an evaporation range of 520-2700 lb. per hour. **The Marshall Organisation, Thermal Engineering Division, Gainsborough.**

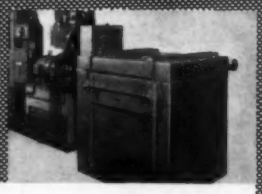
BCE 6226 for further information

P.T.F.E. Flexible Hoses

A newly-marketed flexible hose in P.T.F.E. can be bent to a small radius; for example, 1 in. on a ¼-in. bore tube and 4 in. on a ½-in. bore tube. It can permit misalignment with little risk of fatigue and its smooth bore gives lower frictional losses than some corrugated pattern hoses.

On steam presses P.T.F.E. flexible tubing has achieved well over a million and a quarter movements without serious deterioration. For such duties a working life of the order of 3-5 years is quite possible so that a considerable saving in maintenance costs can be expected. The hose is supplied protected with closely woven wire braiding, and asbestos sheath for insulation can also be provided. Working temperature range is from −80°C (−176°F) to 250°C (485°F), although under certain circumstances it can remain serviceable at temperatures as high as 300°C (572°F). Throughout





"Home-made" LIQUID NITROGEN for research and industry

PHILIPS LIQUID NITROGEN INSTALLATION

- **Produces 4-5 litres (1 gallon) of 99.5 % pure liquid nitrogen per hour or more than 500 litres (110 gallons) per 6 working days;** power consumption at the motor shaft amounts to 6 kW.
- **Full output within 90 minutes from starting-up;** evaporation losses are reduced substantially with the new unit since liquid nitrogen is produced only when needed.
- **The air separation column has no moving parts;** The Philips Gas Liquefier is employed as nitrogen condenser.
- **Special devices ensure nitrogen purity and fool-proof operation;** this means: minimum attention and maintenance.
- **Moisture and carbon dioxide removed by freezing;** no chemicals, no reactivation required.

OTHER PHILIPS CRYOGENIC EQUIPMENT:

Gas Refrigerating Machine
for liquefaction of atmospheric air and other gases; production rate 5 litres of liquid air per hour.

380 litres cold box equipment
for storage, testing or cold treatment of materials from room temperature down to -160° C (-255° F); refrigerating capacity at -100° C: 1110 kcal/hr (4440 BTU/hr) and at -160° C: 640 kcal/hr (2560 BTU/hr) respectively.

PHILIPS

Sales and service organizations all over the world.

Full information about this simple, reliable installation supplied on request by:

N.V. PHILIPS' GLOEILAMPENFABRIEKEN - SCIENTIFIC EQUIPMENT DIVISION - EINDHOVEN - HOLLAND

Sole distributors in the U.K.: Research and Control Instruments Ltd., 207 King's Cross Road - LONDON W.C. 1

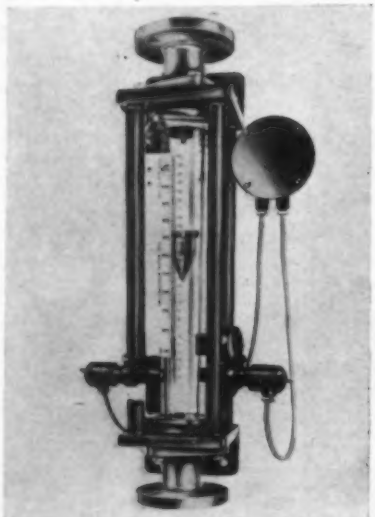
PLANT EQUIPMENT NEWS

the whole temperature range it retains its inherent toughness and has exceptional weathering qualities. Allowable working pressures are 5000 psi for the ¼-in. hose to 2500 psi for the ½ in. hose. At the expense of flexibility very high pressures can be achieved by multi-braiding and some P.T.F.E. hose assemblies have reached 20,000 psi. Robust re-usable brass connections are available. For a corrosive material either a stainless-steel connector can be supplied or a connector incorporating a glass nut and tail. **William Rose Ltd., Hilyn Works, Lockfield Avenue, Brimsdown, Enfield, Middlesex.**

BCE 6227 for further information

Photo-electric Flow Alarm

A flow alarm designed for use with industrial Rotameters Type 907 and 914 consists of a 6-v 6-w bulb as light source and a Mullard ORP11 cadmium sulphide photo-conductive cell. Each of these units is housed in an identical black plastic moulding clamped to diametrically opposite pillars of the chassis. Independent adjustments allow the alarm to be set at the required height and also to align the axes of the lamp and photo-cell centrally through the Rotameter tube. When light from the lamp falls on the photo-cell its resistance falls and allows the passage of sufficient current to operate the relay, coupled to a micro-switch (5A, 230V, A.C. rating). When the Rotameter float obscures the light, the resistance of the photo-cell increases, thus reducing the current, closing the relay and operating the micro-switch, which makes one contact and breaks another.

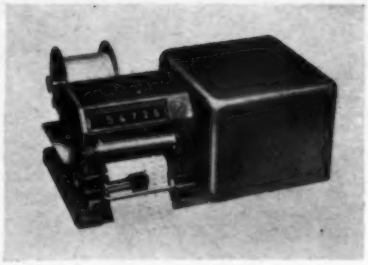


Leads from the lamp and photo-cell are fed to a separate junction box clamped to the chassis. Connection must then be made to the relay box which contains a mains transformer, an alarm relay and a rectifier. **Rotameter Manufacturing Co. Ltd., Purley Way, Croydon.**

BCE 6228 for further information

Electrical Printing Counter

An electro-mechanical counter which provides a permanent printed record of a variety of measurements has been announced by Radiatron. It is available in various models to suit different applications. These include the counting of electrical impulses or closures of a switch up to a speed of 20 a sec., the recording of elapsed time in units of 0.01 min., in seconds, or in one-tenth of a sec., and the counting of revolutions of a shaft up to speeds of 100 a sec. The count is printed in numbers of up to six digits on a paper roll 2⅜ in. wide or on cards. An automatically changed serial number or hand-adjusted code, consisting of figures or letters, can be printed simultaneously and in addition to the counting digits in the same line.



The printing counter measures 11 in. in length, 6 in. in width and 4½ in. in height and weighs approximately 11 lb. It can be supplied with electrical drive operated by a built-in torque motor or with a hand-operated print lever. Printing, paper advance and reset operations are performed by a single action. Alternatively, zero reset may be carried out by a separate lever. **Radiatron, 7 Sheen Park, Richmond, Surrey.**

BCE 6229 for further information

New Publications

Southern Regional Council for Further Education, 8th List. This gives a list of special short courses at Salisbury and S. Wiltshire College of Further Education and at Southampton University. They include sets of lectures on heat and sound insulation, nuclear energy, computers, production and engineering applications of radio isotopes. **22 The Forbury, Reading.**

BCE 6230 for further information

Arthur D. Little Research Institute, Annual Report for 1958. The Arthur D. Little Research Institute, a non-profit-making organisation set up in Inveresk, Midlothian, in March, 1957, to undertake basic research on a contract basis, has just published its second Annual Report reviewing the progress made in 1958. Over one hundred organic compounds have been screened as inhibitors for mild steel, and preliminary attempts have been made to correlate structure and inhibitory power. Further work has been carried out by Dr. Manfred Gordon and his three colleagues on the mechanism and kinetics of the formation of isotactic polymers. A new project is concerned with the chemical modification of wood which will render timber resistant to decay, insects, fire and changes in dimensions without affecting adversely the strength, appearance or any other feature of the wood.

BCE 6231 for further information

Scientific Instrument Manufacturers' Association of Great Britain Ltd. Annual Report and Statement of Accounts for the year ending April 30, 1959, including list of members. This Association now has 136 members and 23 associate members. The report includes notes on the Seventh Annual Convention and on the expanded activities in connection with publicity and advertising. **Sima House, 20 Queen Anne Street, London, W.1.**

BCE 6232 for further information

"Industrial Solvents and Flammable Liquids, 1959." This is a revised edition of a booklet which first appeared in 1954. Intended primarily as a work of reference, the booklet provides information on the physical properties of some 400 liquids—under the heading of flash point, specific gravity, solubility in water, flammability limits, auto-ignition temperature, susceptibility to spontaneous heating and other properties, with recommendations for suitable extinguishing agents. Copies obtainable from the **Fire Protection Association, 31/45 Gresham Street, London, E.C.2.** Price to non-members: 3s.

BCE 6233 for further information

F.P.A. Bulletin, Summer 1959. This issue includes an article on methods of ventilation. Overhead ventilation is appraised. It can encourage the development of fire by causing air movements which can fan a smouldering fire into flames; on the other hand, it can produce improvement in fire-fighting conditions due to the venting of heat and smoke of fire from buildings. The Bulletin is issued to members of the Fire Protection Association (price to non-members: 1s. 6d.). **31/45 Gresham Street, London, E.C.2.**

BCE 6234 for further information

"Platinum-group Metals" briefly describes platinum-metal products including solid and clad platinum metals and alloys in sheet, strip, wire, foil and seamless tubing; parts, shapes and specialists; electrical contacts, electrodes, gauze, catalysts, salts and derivatives, expanded anodes, laboratory ware, rhodium plating solutions, transistor materials and thermocouple wire. Typical clad metal combinations, thermocouple wire compositions, catalyst forms and the stock of salts maintained are listed. **Metals & Controls, Division of Texas Instruments Inc., 34 Forest Street, Attleboro, Massachusetts, U.S.A.**

BCE 6235 for further information

BCE 6147 for further information

So simple!

So surely SIMPLIFIX the foolproof coupling!

Simplifix couplings form a perfect joint on almost any kind of tubing including those with very thin walls. All that is required is tightening with a spanner – no special work is required on the tube and the anti-friction washer prevents the tube twisting when the nut is tightened. Simplifix couplings are suitable for all pipe line systems up to 2″ o.d. In a wide range of interchangeable standard fittings. Non-standard fittings of all kinds can also be made to order. Write for further information and fully illustrated catalogue.

SIMPLIFIX

SIMPLIFIX COUPLINGS LIMITED
HARGRAVE ROAD · MAIDENHEAD
BERKS · TEL: MAIDENHEAD 5100
A member of the ALENCO Group of Companies

Month's News in Brief

Factory Equipment Exhibition for Manchester

The next Factory Equipment Exhibition, the eighth of a very successful series, will be organised by Industrial & Trade Fairs Ltd., the exhibition company jointly owned by *The Financial Times* and the George Newnes group of companies, who have acquired the full rights of this important industrial exhibition.

In future, this exhibiton wll be sponsored jontly by *The Financial Times* and *Industrial Equipment News* (published by the Tothill Press Ltd.). Next year (1960) it will open on September 21, at Belle Vue, Manchester, and in 1961 it will be held at Earls Court, London, thus establishing a pattern of alternate displays in London and the heart of the industrial north.

Among the engineering bodies supporting the exhibitions are the Institution of Mechanical Engineers, the Institution of Electrical Engineers and the Institution of Production Engineers.

Attendance has steadily grown each year, and the audited figure of 51,124 for 1959 reveals an average daily attendance of over 5,000. Analysis of ticket applications showed that the big bulk of visitors belonged to one of three main groups in this order:

(1) managing directors, works directors and factory managers (nearly 40%);
(2) purchasing officers, office managers, welfare - safety - personnel officers, stores control, costing and other executives (over 30%);
(3) plant engineers, production and development engineers (nearly 30%).

One of the innovations of the 1960 exhibition will be the grouping of the various categories of the several hundred different types of exhibits. Equipment and services for which there will be special sections include: handling and storage, insulation, protective clothing, air conditioning, instruments and electronic controls, welfare and safety, cleaning and maintenance, product finishing, machines and tools, heating and ventilation, drawing-office equipment, business systems and production controls, dust and fume extraction, construction and partitioning, packaging and packing.

British Titan Developments Abroad

In addition to the plans for expansion of home-based plant for the manufacture of pigment, which will result in an increase in capacity of from 70,000 tons to 105,000 tons per year, a number of other developments away from home have been announced by British Titan Products Ltd. The total sum involved is £14 million.

For example, in Australia, the plant of the company's wholly owned subsidiary Australian Titan Products at Burnie, Tasmania, has been continuously expanded since it was opened in 1949 and the output is to be raised from 8000 to 10,000 tons p.a. by the end of 1959. Early in 1962 the capacity will have been increased to 16,000 tons p.a. Still further extensions will increase this to 22,000 tons p.a. by about the end of 1964.

In India B.T.P. have a substantial minority holding in Travancore Titanium Products and at the Trivandrum plant of this latter undertaking output is expected to rise from 1800 to 3600 tons per annum by 1962.

In South Africa, B.T.P., in association with African Explosives & Chemical Industries Ltd., are to establish a plant at Umbogintwini, near Durban. This plant is expected to be completed in about 1962 and will have a capacity of 10,000 tons p.a. Sulphuric acid and steam will be drawn from the works of A.E. & C.I., and ilmenite—the mineral source of titanium oxide—from the neighbouring mines at Umgababa which are already supplying very substantial tonnages to B.T.P.'s plants in England.

Even more ambitious plans are destined for Canada, where sales of British Titan Products have been steadily rising since 1950. In that year 19% of the titanium oxide sold in Canada came from B.T.P. By 1957, B.T.P.'s share had grown to 49% of the market in competition with the best U.S.A. producers. This increase does not tell the whole story, because, during this period, the total market in Canada itself had grown. B.T.P. sales in 1957 were four times the 1950 total and represented a very high proportion of the U.K.'s exports of chemical products to Canada.

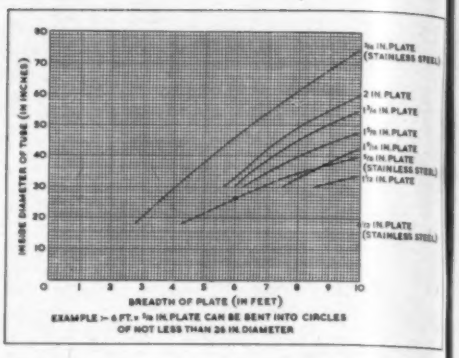
B.T.P. has now decided to establish a company in Canada and will erect a plant there at a cost of some £6 million. It is planned to have an initial capacity of 20,000 tons p.a.; both Rutile and Anatase will be produced and the plant is being designed to allow for big future extensions. The location has not yet been fixed. The plant will be a self-contained unit, making its own acid and manufacturing titanium oxide from titanium slag which is already produced in Canada.

The Chairman of British Titan Products, Mr. Beethby, has intimated that his company is the largest producer of titanium pigments outside the U.S.A., a position which the company has every intention of retaining.

New Factory for Heat Exchangers and Pressure Vessels

First-class facilities for the design and manufacture of all kinds of chemical plant, including pressure vessels and heat exchangers, will shortly be available to industry through the new factory now nearing completion on the Crown Works site of Steels Engineering Installations Ltd., the Sunderland engineering enterprise.

The equipment now in course of installation comprises the most modern of its kind available for fabrication purposes and with very adequate capacity. Thus, the plate rolling plant includes a pyramid rolling machine which will, for instance, roll ½ in. thick 10 ft wide stainless-steel plate down to a diameter of 18 in. and a 2 in. by 5 ft 6 in. mild steel plate to a minimum inside diameter of 2 ft 6in. More details of these capacities will be found on the accompanying graph; but, whilst the diameters quoted are the minimum possible, it will be appreciated that there is no maximum limit.


INSIDE DIAMETER OF TUBE (IN INCHES)
BREADTH OF PLATE (IN FEET)
EXAMPLE :- 6 FT. × 5/8 IN. PLATE CAN BE BENT INTO CIRCLES OF NOT LESS THAN 28 IN. DIAMETER

In the plating shop, where marking-out, edge planing, edge setting and plate rolling will be carried out, cutting will be performed by automatic oxy-acetylene cutters. Some of these machines will make straight cuts, others will cut circles for such parts as dished and flanged ends, tube plates and reinforcing rings. All machines will cut mild steel of any thickness and stainless steels in thicknesses up to 7 in., all at high speeds. The planing machinery will handle plate up to 35 ft in length, and edge setting will be carried out by means of a 900-ton hydraulic press.

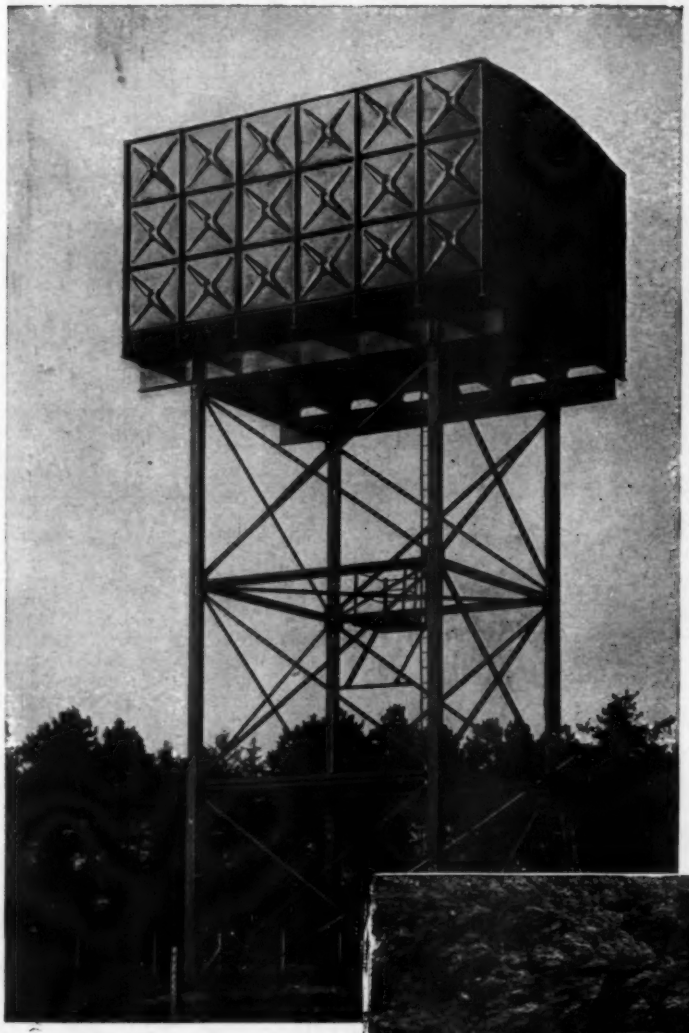
In the assembly bay welding will be carried out with a 1200-amp. d.c. type automatic welder which can handle both the main longitudinal and circumferential seams of a vessel. Large nozzles and flanges can be welded to dished ends heads by the same machine.

It will be possible to stress-relieve large vessels at this factory and all welded joints can be radiographed to meet the requirements of the various codes.

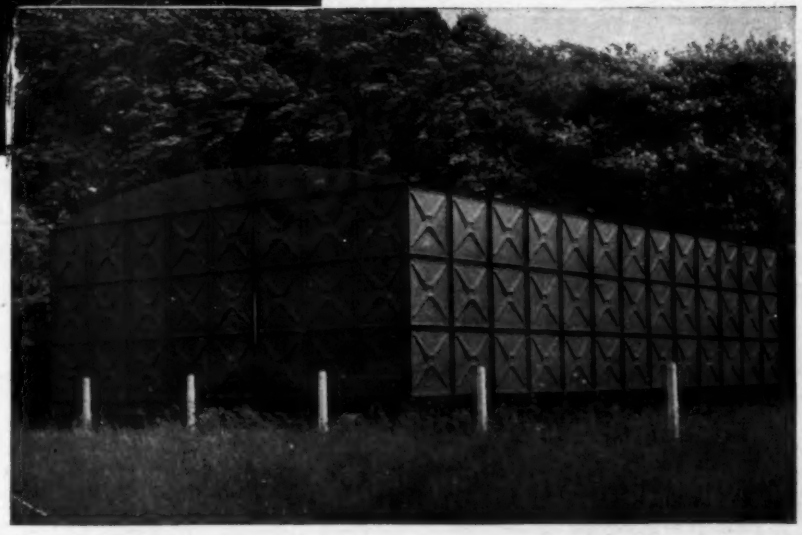
News Briefs

Recently the formation of a new international company to serve the petroleum and chemical industries was announced jointly by Arthur G. McKee & Co. of Cleveland and Head Wrightson & Co. Ltd. of Thornaby-on-Tees, England.

The new concern, McKee Head Wrightson Ltd., will be a British company with headquarters in London. It will combine the experience of the two parent firms in the designing, engineering and building of petroleum refineries and chemical plants throughout the world exclusive of the North American continent.



Braithwaite PRESSED STEEL SECTIONAL TANKS



Braithwaite Pressed Steel Tanks with external flanges throughout comply with British Standard 1564 : 1949. The sectional method of construction enables tanks with an unlimited range of capacities to be provided. Suitable for the storage of most liquids and viscous substances, they can be economically transported and erected in positions inaccessible to other forms of construction. They can also be increased in size when additional capacity is required. Illustrated brochure will be sent on application.

Selling Agents

THOS. W. WARD LIMITED

ALBION WORKS · SHEFFIELD

TELEPHONE: 26311 (22 LINES) · TELEGRAMS: "FORWARD · SHEFFIELD"

LONDON OFFICE: BRETTENHAM HOUSE · LANCASTER PLACE · STRAND · W.C.2

BT/25.

Ownership of the company will be shared equally by McKee and Head Wrightson. The two companies have been associated for the last 15 years in contracting for the steel industry in the British Commonwealth. This association, which is independent from the petroleum and chemical operations of the new company, will continue. Also, the parent companies emphasised that each would continue its own individual activities as heretofore.

Compoflex Co. Ltd., manufacturers of flexible tubing and hoses, announce the opening of a London warehouse at Angel House, Pentonville Road, London, N.1 (telephone Terminus 0533/4), where stocks will be held to provide speedier distribution to customers in London and the Home Counties. Included in these stocks will be a range of Pirelli long-length moulded rubber hoses.

Crude oil production from BP Exploration Co.'s English oilfields totalled 39,827 tons in the first half of 1959. This compared with a production of 40,101 tons in the first six months of 1958. The main producing fields are at Eakring and Egmanton (Notts.) and Plungar (Leics.).

BP Exploration Co. is making good progress in the development of the three new oilfields at Bothamsall, in Nottinghamshire, and Gainsborough and Corringham, in Lincolnshire, which it discovered last year. At the Bothamsall field five successful producing wells have now been completed. Probably some 20 to 30 wells will have been sunk when this field is fully drilled up.

Texas Instruments Ltd., British associates of Texas Instruments Inc., have announced the first details of their new plant which is to be built at Mantons Lane, Bedford.

The new building will have a manufacturing area, in the form of a hollow square, of 100,000 sq. ft. In Stage 1 only 67,000 sq. ft of this block is being constructed, leaving the mirror image completing the square to be added at a later date.

People in the News

The British Oxygen Group of Companies announce the award of the following fellowships for postgraduate research training. **Mr. J. P. Catchpole**, of Birmingham University, for research training in the Department of Chemical Engineering, Birmingham University. **Mr. R. M. Thorogood**, of Imperial College, for research training at Imperial College, London. Renewal of the fellowship for a third year has been granted to **Mr. R. D. Johnston** for research training at Battersea Polytechnic.

Cyanamid International announce that **Dr. Robert F. Hudson**, at present a lecturer in chemistry at the University of London, has been appointed a group director of research at Cyanamid's Research Institute, Geneva. He will take up his appointment early in 1960. **Dr. Volker Franzen**, of Heidelberg, has also been appointed to a similar post. Announcing the appointments, Dr. R. C. Swain, President of the Institute and Vice-President for Research and Process Development of the parent corporation, American Cyanamid Co., said that both scientists would pursue their investigations with a free hand, directing their work towards the uncovering of new scientific information rather than towards the development of specific commercial products. He added: "The aim of the Institute is to take full advantage of European methods for conducting research. There will be no American on the full-time staff."

Dr. Robert F. Hudson. *Mr. N. R. Kirby.*

Mr. N. R. Kirkby, who has just been appointed general sales manager of Croda Ltd., the chemical, oil and paint manufacturers, will be making a tour of Croda's continental associates next month. Mr. Kirkby, who joined Croda 20 years ago as a laboratory assistant, has for the past few years been the company's chief technical representative in the Sheffield area. He will now take charge of Croda's entire sales organisation. **Mr. R. J. Seddon** will be succeeding Mr. Kirkby as Croda's representative in the Sheffield area.

The Scientific Instrument Manufacturers Association of Great Britain announced recently the inauguration of SIMA's new director, **Capt. Robert Alexander Villiers**. Capt. Villiers commanded at one stage in an eventful and distinguished career the Underwater Countermeasures and Weapons Establishment of the Royal Navy at Havant, a research and development establishment.

Forthcoming Events

Institution of Chemical Engineers

October 6. *At London.* At the Geological Society, Burlington House, W.1. "The Controlled Crystallisation of Sodium Chloride" by J. Bain and F. Rumford. **5.30 p.m.**

October 7. *At London.* Meeting of the British Nuclear Energy Conference sponsored by the Joint Panel on Nuclear Marine Propulsion at the Institution of Naval Architects, 10 Upper Belgrave Street, S.W.1. "Nuclear-powered Dry Cargo Ships" by E. C. B. Corlett and E. P. Hawthorne. Requests for further information should be made to the sponsoring bodies and not to the Institution.

October 22-23. *At London.* A Symposium on Utilities and Services in the Chemical Industry (Students and Graduates Section), at the Hotel Russell, W.C.1.

The Graduates and Students section of the Institution of Chemical Engineers are performing a commendable service with their organisation of the above conference. This will last for two days, October 22 and 23, and will have a wide coverage of subject-matter.

1. "The Choice of Fuels and Plant for Steam Raising in the Chemical Industry" by H. A. Cameron, M.I.Mech.E.—Babcock & Wilcox Ltd.
2. "The Balance between Power and Process Steam Requirements" by E. T. Moss, Ph.D., D.I.C., A.C.G.I., M.I.Chem.E. — Tate and Lyle Research Laboratory, Kent.
3. "The Efficient Use of Process Steam" by R. Clare, B.Sc., M.Inst.F. —National Industrial Fuel Efficiency Service, London, W.1.
4. "Treatment of Industrial Waters" by D. Billingham, M.A.—Assistant Service Manager, I.C.I. "Afloc" Water Treatment Service, London, S.W.7.

(These papers are to be read on the 22nd.)

5. "Industrial Cooling Towers, including New Design Methods and Materials of Construction" by D. J. Tow, B.Sc.(Eng.), Dip.Chem.Eng. (U.C.L.), A.M.I.Mech.E., A.M.I.Chem.E. — Deputy Commercial Manager, Head Wrightson Processes Ltd., London, E.C.1.
6. "Air Cooling of Condensers and Heat Exchangers" by R. V. Macbeth, B.Sc.(Eng.), D.I.C. Ph.D., A.M.I.Mech.E. — Project Engineer, Imperial Chemical Industries Ltd., Billingham Division, Co. Durham.
7. "Techniques and Equipment for the Use of Heat Transfer Agents" by A. P. Shahbenderian, B.A.—Chemical Engineering Laboratories, University of Edinburgh and Heriot-Watt College, Edinburgh, 1.
8. "Costs of Utilities and Services" by R. S. Bickle, B.A. (Cantab.), A.M.I.Chem.E.—Carbonisation Department, National Coal Board, London, S.W.1.

Society of Instrument Technology

The meetings below will be held at Manson House, 26 Portland Place, London, W.1, at 6.30 for **7 p.m.**

October 27. "Modern Developments in Optical Instruments", J. H. Bach, B.Sc., and G. E. Fishter.

November 24. "Application of Instrumentation to Glass Melting Furnaces", N. I. Walker.

Bristol Section

To be held at the University of Bristol, Physics Department, at **7.30 p.m.**

October 15. "An Ultrasonic Flowmeter", R. E. Fischbacher, B.Sc., A.R.T.C., A.M.I.E.E.

Other Meetings

October 6. *At Livingstone Hall, Broadway, London, S.W.*1. One-day conference on Planned Maintenance. Further details from The Secretary, Harrow and Wembley Productivity Association, Kodak Ltd., Harrow, Middlesex.

October 7. *At Queens Hotel, Birmingham.* "Titanium and its Alloys for Chemical Plant". Organised by the Institution of Engineering Designers. **7.30 p.m.**

October 20-23. Clean Air International Conference and Exhibition at Seymour Hall, London. Further information from National Society for Clean Air, Palace Chambers, Bridge Street, London, S.W.1.